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Technical Report #27

Electrochemical Parameterization of Metal Complex Redox Potentials, using the Ruthenium(III)-Ruthenium(II) Couple to generate a Ligand Electrochemical Series.

By

A.B.P. Lever

in
Inorganic Chemistry

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SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

1a. REPORT SECURITY CLASSIFICATION		1b. RESTRICTIVE MARKINGS	
2a. SECURITY CLASSIFICATION AUTHORITY Unclassified		3. DISTRIBUTION/AVAILABILITY OF REPORT As it appears on the report	
2b. DECLASSIFICATION/DOWNGRADING SCHEDULE			
4 PERFORMING ORGANIZATION REPORT NUMBER(S) Report # 27		5. MONITORING ORGANIZATION REPORT NUMBER(S)	
6a. NAME OF PERFORMING ORGANIZATION A.B.P. Lever, York University Chemistry Department	6b. OFFICE SYMBOL (If applicable)	7a. NAME OF MONITORING ORGANIZATION Office of Naval Research	
6c. ADDRESS (City, State, and ZIP Code) 4700 Keele St., North York, Ontario M3J 1P3 Canada		7b. ADDRESS (City, State, and ZIP Code) Chemistry Division 800 N. Quincy Street Arlington, VA 22217 U.S.A.	
8a. NAME OF FUNDING/SPONSORING ORGANIZATION	8b. OFFICE SYMBOL (If applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER N00014-84-G-0201	
8c. ADDRESS (City, State, and ZIP Code)		10. SOURCE OF FUNDING NUMBERS	
		PROGRAM ELEMENT NO	PROJECT NO
		TASK NO	WORK UNIT ACCESSION NO
11. TITLE (Include Security Classification) Electrochemical Parameterization of Metal Complex Redox Potentials, using the Ruthenium(III)/Ruthenium(II) Couple to generate a Ligand Electrochemical Series.			
12. PERSONAL AUTHOR(S) A.B.P. Lever			
13a. TYPE OF REPORT Technical	13b. TIME COVERED FROM Aug. 89 to Aug. 90	14. DATE OF REPORT (Year, Month, Day) October 20, 1989	15. PAGE COUNT 49
16. SUPPLEMENTARY NOTATION			
17. COSATI CODES		18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) Electrochemistry, Parameterization, Ligand Series, Ruthenium	
19. ABSTRACT (Continue on reverse if necessary and identify by block number) > A ligand electrochemical parameter, $E_L(L)$, is described to generate a series which may be used to predict $M(n)/M(n-1)$ redox potentials by assuming that all ligand contributions are additive. In this fashion it performs a similar purpose to the D_q parameter in electronic spectroscopy. The parameter is defined as 1/6 that of the Ru(III)/Ru(II) potential for species Ru ⁶⁺ in acetonitrile. The $E_L(L)$ values for over 200 ligands are presented and the model is tested over a wide range of coordination complexes and organometallic species. The redox potential of a $M(n)/M(n-1)$ couple is defined to be equal to - $E_{red} = f[\sum E_L(L)] + C$. The values of f and C , which are tabulated, depend upon the metal and redox couple, and upon spin state and stereochemistry, but, in organic solvents, are generally insensitive to the net charge of the species. Consideration is given to synergism, the potentials of isomeric species, and the situations where the ligand additivity model is expected to fail. In this initial study, the redox couples are restricted almost exclusively to those involving the loss or addition of an electron to the t_{2g} (in O_h) sub-level.			
20. DISTRIBUTION/AVAILABILITY OF ABSTRACT <input checked="" type="checkbox"/> UNCLASSIFIED/UNLIMITED <input type="checkbox"/> SAME AS 3a <input type="checkbox"/> DDCI USES		21. ABSTRACT SECURITY CLASSIFICATION Unclassified/unlimited	
22. NAME OF RESPONSIBLE INDIVIDUAL Dr. Robert K. Grasselli		23. TELEPHONE (Include Area Code)	
DD FORM 1473, 34 MAR		33 APR edition may be used until exhausted All other editions are obsolete	
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Electrochemical Parameterization of Metal Complex Redox Potentials, using the Ruthenium(III)/Ruthenium(II) Couple to generate a Ligand Electrochemical Series.

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Abstract

A ligand electrochemical parameter, $E_L(L)$, is described to generate a series which may be used to predict $M(n)/M(n-1)$ redox potentials by assuming that all ligand contributions are additive. In this fashion it performs a similar purpose to the Dq parameter in electronic spectroscopy. The parameter is defined as 1/6 that of the Ru(III)/Ru(II) potential for species RuL in acetonitrile. The $E_L(L)$ values for over 200 ligands are presented and the model is tested over a wide range of coordination complexes and organometallic species. The redox potential of a $M(n)/M(n-1)$ couple is defined to be equal to:- $E_{cell} = f[\sum E_L(L)] + C$. The values of f and C , which are tabulated, depend upon the metal and redox couple, and upon spin state and stereochemistry, but, in organic solvents, are generally insensitive to the net charge of the species. Consideration is given to synergism, the potentials of isomeric species, and the situations where the ligand additivity model is expected to fail. In this initial study, the redox couples are restricted almost exclusively to those involving the loss or addition of an electron to the t_{2g} (in O_h) sub-level.

Introduction

In the mid 1970s there appeared a series of papers dealing with the possibility of correlating electrochemical (oxidation) potentials with HOMO energies and ligand substitution effects.

Treichel and co-workers^{1,2} demonstrated that in a series of manganese carbonyl isocyanide derivatives successive replacement of CO by MeCN raised the oxidation half-potentials by 0.5V per ligand substituted. Sarapu and Fenske³ further showed that these changes in half-potentials upon ligand substitution were linearly correlated with the HOMO energy (from which orbital oxidation occurred) as calculated by the non-empirical Fenske-Hall MO analysis. Parallel studies by Pickett and Pletcher^{4,5} also with general complexes of the type $[M(CO)_{8-n}L_n]^{y+}$ led them to introduce the equation:

$$E_{ox} = A + n[dE^o/dn]_L + Cy \quad (1)$$

where dE^o/dn is the change in potential upon replacement of nCO by n ligands, E_{ox} is the metal oxidation potential and A and C are constants.

This relationship does not permit a distinction to be made between isomeric pairs of complexes such as cis and trans-ML₄L'z and this led to the development of rather more complex relationships which, in the case of the carbonyl complexes were related to how many of the metal dπ orbitals overlapped carbonyl π* orbitals.^{6,7}. This area has recently been reviewed⁸.

Subsequently, there have been a relatively small number of papers⁹⁻¹⁵ which have developed these equations and utilised ligand parameters, P_L , where $P_L = dE^o/dn$ initially being defined⁴ as:-

$$P_L = E_{1/2}[Cr(CO)₈] - E_{1/2}[Cr(CO)₅L] \quad (2)$$

There has not been widespread use of this approach since P_L values are known for relatively few ligands. Its lack of use may also be because it was seen to be of value to organometallic chemistry, rather than to coordination chemistry in general.

However, the common basis of this approach is the concept that electrochemical potentials are additive with respect to ligand substitution, at least with respect to substituted metal carbonyls. In this paper we explore the premise that this is in fact a very general observation, common to both organometallic and coordination chemistry. Indeed we demonstrate that, for a wide range of different complexes, electrochemical potentials are additive with respect to ligand variation and we discuss well defined and predictable situations where this is not the case.

Assuming ligand additivity to be widely justifiable, the intent is to define a ligand electrochemical parameter which, in the fashion that D_q defines the crystal field electronic spectrum of a metal complex, would permit the definition of the redox energies of a metal complex.

An important implication of such a parameter is the conclusion that all ligands would behave in the same relative way to many metal redox couples, be the ligands hard or soft, and this observation would require some rethinking of our chemical bonding models and concepts.

We introduce an electrochemical standard based upon the change in the ruthenium(III)/ruthenium(II) couple in organic solvent (usually acetonitrile), as a function of bound ligand. A new set of ligand parameters, E_L , are proposed which have broad utilisation across both organometallic and coordination chemistry, with values for over 200 ligands being currently defined here.

Previously there have been many studies relating electrochemical potentials to a wide range of other properties such as charge transfer transition energies, photoelectron binding energies, kinetic parameters, and many different infrared

vibrational frequencies, such as CO, N₂ and M-H stretching frequencies, etc.⁸. Thus the EL parameter has the promise of wide applicability. A preliminary report of this method has been made¹⁶. Haga and co-workers¹⁷ have recently noted the additivity of ligand contributions to ruthenium(III)/ruthenium(II) potentials in some mixed bidentate amine ruthenium complexes, while, earlier, Tfouni and co-workers¹⁸ noted similar behaviour for some ruthenium complexes in aqueous medium.

Data are restricted to electrochemically reversible or, at least, quasi-reversible redox couples involving the metal ion, M(n)/M(n-1). Data in this paper refer almost exclusively to redox processes occurring within the non-bonding or weakly π-bonding (or anti-bonding) t_{2g} (in octahedral) sub-set. This procedure should be used with caution in situations where; a) there are extraordinary synergistic interactions between metal and ligand, b) the potentials are significantly solvent dependent because of a special solvent interaction, c) strong covalent interaction leads to "non-innocent" behavior, or "non-innocent" ligands are present, e.g. NO, d) equilibria are present such that the potential of a complex, in either oxidation state M(n) or M(n-1), say ML_xY_y depends upon the bulk concentration of L or Y, e.g. where L and/or Y are solvolysed rapidly, or where, for example, a supporting electrolyte ion, X⁻ might displace L or Y, or in general any preceding or following coupled chemical reaction which significantly changes the inner shell environment of the metal ion in either oxidation state, e) the additivity contribution of a bulky ligand depends upon possible steric interactions with other co-ligands and f) for example the hole size in a macrocycle is fixed and therefore will be an important factor in determining the metal ligand binding energy, e.g. the metal may be in or out of the plane. While exercising caution in this respect, the deviation of the observed from calculated potential may provide useful energy information concerning, for example, synergism or non-innocence etc.

Redox couples involving ligand processes are not included but there is evidence that these are related to metal couples¹⁹ so that these may ultimately be included.

Experimental

All the electrochemical data discussed here, drawn from the previous literature as appropriately referenced in the Appendix, are cited against NHE. Where other standard electrodes (SCE, SSCE, AgCl/Ag etc.) were used the data were corrected according to Bard and Faulkner.²⁰. Many authors added ferrocene as an internal reference to their electrochemical cell. To correct to NHE, the ferrocenium/ferrocene couple is assumed to lie at 0.665V vs NHE in acetonitrile.²¹

Results and Discussion

A Standard Electrochemical Data Set

A standard parameter set should:-

- i) be based upon a single standard redox process of a metal center,
- ii) be available for a very wide range of compounds by variation of ligand.
- iii) be electrochemically reversible or quasi-reversible.
- iv) be relatively solvent and supporting electrolyte independent.
- v) have potentials which are largely independent of the net charge on the molecule in organic solvents and
- vi) be largely independent of isomerism (cis/trans, mer/fac etc.)

The set of compounds [Ru(bpy)_nX_(8-2n)]²⁺ (n=0-3), (bpy = 2,2'-bipyridine) where X may represent monodentate or polydentate ligands, meet criteria (i-vi) par excellence and an extraordinarily large number are known.^{19,22,23}. These formed the initial basis set from which the ligand parameters could be derived. The relevant redox process is the Ru(III)/Ru(II) couple and electrochemical information exists for over 200 different ligands, for these complexes, mostly collected in acetonitrile.

The "Bu(bpy)₃]²⁺ cation was first considered; its Ru(III)/Ru(II) potential

occurs at 1.53V vs NHE average reported potential in acetonitrile solution.²⁴ Since this complex contains six identical Bu-N bonds, the Eu contribution for 2,2'-bipyridine was first defined to be 1.53/n = 0.255V.

In the complex [Ru(bpy)_nCl_{2-n}]^{m+}, (n = 0-4), with potential E_{obs}, the Eu value for ligand L, Eu(L), was derived such that:-

$$E_{obs}(\text{Ru(III)/Ru(II)}) = (2n * 0.255) + (6-2n) * \text{Eu}(L) \quad (3)$$

In general one may have data for complexes of the type Ru(bpy)₂L_x and Ru(bpy)₂L_x providing two independent evaluations of Eu(L), once a value for Eu(bpy) is assumed. Values for RuL_x where available, (where L may also be L₂'s bidentate etc., are also included in the data set, providing three independent evaluations for Eu(L). In this fashion Eu values for over 100 ligands were initially defined. Subsequently other values for L other than 2,2'-bipyridine were used to define the best (least squares) average value for Eu(2,2'-bipyridine) using a database of 84 ruthenium bipyridine complexes - this final average value of Eu(2,2'-bipyridine) = 0.259 V then became the primary electrochemical standard value against which all other ligand values were subsequently re-evaluated. The ruthenium data base was then expanded to include Ru(III)/Ru(II) couples in a range of well defined species, not restricted to those containing 2,2'-bipyridine.

Generally, several values for Eu(L) for a given ligand were determined from the Ru(III)/Ru(II) couples of the general complexes RuX_xY_yZ_z, assuming ligand additivity for X, Y and Z. The averages of these values (which usually do not differ by more than 20mV) are listed, for a large range of ligands, in Table 1. Ligands showing larger variations from one complex to another, are indicated by (#) in Table 1 and are discussed in more detail below.

Thus for [RuX_xY_yZ_z], the calculated potential, E_{calc}, (in acetonitrile), using the Eu(L) data presented in Table 1, is given by:-

$$E_{calc} = x * \text{Eu}(X) + y * \text{Eu}(Y) + z * \text{Eu}(Z) \quad (4a)$$

$$= \Sigma a_i \text{Eu}(L_i) + [NE_L] \quad (\text{in abbreviation}) \quad (4b)$$

The extent to which ligand additivity is valid in ruthenium complexes is shown in Fig.1, where the observed versus calculated potentials for 103 mixed ligand ruthenium complexes (which were not included in the basis set to define Eu(L)) are displayed. Supporting electrolyte effects are generally small.^{24,25} d-levant effects in Ru(III)/Ru(II) couples are also generally very small where different organic solvents are concerned, though with some exceptions.²⁶⁻²⁸ Nevertheless where possible, data recorded in acetonitrile, a very common electrochemical solvent, are utilised. The actual calculated and observed values for these and all other displayed data are collected in the Appendix. Ideally the best line through this data set should have a slope of unity and pass through the origin. In fact the equation of the best line is (Table 2):-

$$E_{obs} = 0.97 [NE_L] + 0.04 \quad (\text{V}) \quad R = 0.89 \quad (5)$$

Within the ruthenium series, with few exceptions, there is little difference in potential between pairs of isomers. Moreover, the good correlation shows that the overall net charge on the complex plays little role, at least in acetonitrile, in determining the observed redox potential.

These data were collected from the literature. Erroneous data may have been reported if inadequate care had been taken concerning the purity (especially organo-

of solvents, the electrochemical cell design, the quality of the reference electrode and the fact that where organic solvents are concerned excessive cell resistance can lead to appreciable iR drop thereby leading to error, as indeed is the present case. Junction potentials. Moreover data are reported against a variety of reference electrodes including NHE, SCE, SSCE, ferri-ferrocene and several different silver based couples. While, in this collection, data are corrected to a common electrode, NHE, it is evident that the experimental values are subject to some error and the scatter in this line (and those presented later) (Fig.1) may reflect such experimental limitations as much, or more, than it reflects breakdown in ligand additivity.

Correlation with Previous Ligand Parameters

The Ru(III)-Ru(II) data set should correlate with parameters previously introduced by Fickett and co-workers and developed particularly by Fomichev.¹² In Fig.2 shows a plot of the previous ligand parameters, P_L , versus E_L - the correlation is clearly linear except for carbon monoxide to which we return below. The relationship between these parameters is given by (Table 2):-

$$E_L = 1.17 P_L + 0.86 \quad (\text{V}) \quad R = 0.98 \quad (6)$$

for 17 ligands.

This correlation is used to derive values of E_L where the P_L value is known but where there are no appropriate ruthenium complexes from which to derive E_L . Such values are annotated as PPLC in Table 1.

Extension to Ruthenium Data in Water.

The Ru(III)/Ru(II) potentials of many ruthenium complexes have also been recorded in water. When compared with the values calculated using eqn.(4), being those which would be observed in acetonitrile, there is a small but significant shift in potential. In Fig.1 is shown a plot of the potential calculated using expression (4), (or in some cases observed directly in acetonitrile) and the observed potentials in water.

A straight line correlation is observed for the large set of net +2 charged species, given by:-

$$E_{\text{obs}} \text{ Ru(aq)}^+ = 1.14 [E_L] - 0.35 \quad (\text{V}) \quad R = 0.97$$

7.

The correlation line characteristics for this and subsequent plots are listed in Table 2; both regression and standard error data are included. The significance of the values of slopes and intercepts is discussed below. Data for a limited number of '+1' species are also plotted in Fig. 1 and appear, perhaps fortuitously, to lie on the same line. A small group of complexes of net charge zero do not appear to fall on this line (vide infra). In general, data in water may be rather more scattered than those collected in a common organic solvent because of the variation in solute concentration and pH. For some ligands, ruthenium redox data are available in water not in the organic solvent. In these cases E_L values are calculated from eqn.(4) and are included in Table 1 (annotated as [aq]).

Comparison with Other Electrochemical Data Sets

It is necessary to demonstrate that these E_L - L parameters may be used to predict other metal ions in a range of oxidation states, and are not restricted to the Ru(II) and closely related metal ions such as Os(IV).

Thus we plot the observed potentials for any M^{n+} - M^{n+} couple for the

species $M_xY_yZ_z$, against those calculated using eqn.(4), to obtain what we refer to here as an El plot. Least squares analysis to fit calculated to the observed data yields the equation:-

$$\begin{aligned} E_{\text{obs}} &= f[\Sigma \text{EL}(L_i)] + C \\ &= f[\Sigma \text{EL}] + C \end{aligned} \quad (8)$$

to derive f and C for the specific couple $M(n)/M(n-1)$ in the species $M_xY_yZ_z$.

For any given $M(n)/M(n-1)$ couple, ALL complexes of given stereochemistry and spin state, should fall on the same correlation line, i.e. have the same slope f and intercept C . Using the Fe(III)/Fe(II) couple, by way of example, one expects that all species where the Fe(III) complex is six coordinate and low spin, and the Fe(II) complex is six coordinate and low spin, will fall on the same correlation line. However species where, for example, both the iron oxidation states form high spin six coordinate complexes will generally have a different value for f and C , than for the aforesaid line. Similarly if the Fe(III) species is low spin, but the Fe(II) species is high spin, yet another correlation line may be generated.

Thus for each oxidation state couple $M(n)/M(n-1)$, a series of correlations may exist if there is variability in stereochemistry and/or spin state. This follows because the observed redox potential is a measure of the relative binding constants for the ligands with $M(n)$ and with $M(n-1)$, and such binding constants will generally depend upon both stereochemistry and spin state.

Consider first a series of osmium complexes (Os(III)/Os(II) couple), where it is not surprising that an El plot shows an excellent correlation (Fig.3); indeed it has been previously demonstrated that the corresponding potentials for analogous ruthenium(II) and osmium(II) species are linearly related.²⁴ There is also a good correlation for aqueous phase osmium(III)/osmium(II) data (Fig.3). Table 1 includes a few ligands derived from osmium data and the appropriate correlation line (Table 1), where such data were not available from ruthenium species. They are annotated [Ps].

The El plot for the Cr(III)/Cr(II) data set (low spin Cr(II)) shown in Fig.4 illustrates a comparison of the observed Cr(III)/Cr(II) couples for a variety of chromium complexes, in organic solvents, with a notation indicating their net charge of the lower oxidation state species here and henceforth). The reasonable linearity of this plot shows that these chromium data are fairly well behaved vis-a-vis ligand additivity. Note that the (+2), (0) and (-2) species all lie on the same line and thus the relative unimportance of net charge is demonstrated. Fig.4 also shows corresponding organic solvent data for high spin chromium(II) species, (charge -1, +1, +2)) with the slope and intercept differing from those of the low spin species.

In water solvent (Fig.5), an excellent line is observed for all the low spin chromium(II) net charge (2+) species; the $[\text{Cr}(\text{CN})_6]^{4-}$ species also lies on this line though this is rather unexpected and may be fortuitous (see further comment below).

Similar data are observed with iron. Fig.6 shows how the Fe(III)/Fe(II) potential, as measured in an organic solvent, of a series of six coordinate iron(II) complexes (low spin Fe(II) and Fe(III)) depends upon their El sum. There is clearly a linear correlation independent of charge. Thus for the $(\text{L}_2)\text{Fe}(\text{III})/(\text{L}_2'\text{Fe}(\text{II}))$ couple illustrated in Fig.5, the least squares equation is:-

$$V_{\text{Fe}} = 1.11[\Sigma \text{EL}] - 0.43 \quad (\text{V}) \quad R = 0.98 \quad (9)$$

This equation should be appropriate for ALL iron complexes in organic solvent, provided that both the iron(II) and iron(III) complexes are low spin octahedral and

generally excluding situations as defined in the Introduction. Six coordinate high spin complexes ($\text{Fe(III)}/\text{Fe(II)}$ couple, both high spin) in organic solvents, exhibit potentials which fall on a different line (Fig.6).^{29,30} Thus these two lines (Fig.6, 2) should provide the means of predicting the $\text{Fe(III)}/\text{Fe(II)}$ potentials for most six coordinate iron complexes, in organic solvents.

In water (Fig.5) some (low spin $\text{Fe(II)}, \text{Fe(III)}$) charged species have potentials which fall on a line which is apparently defined by a group of ± 2 net charge species and the range of $[\text{Fe}(\text{CN})_6(\text{R-Py})]^{3-}$ species (vide infra). Species of 4 and - charge fall somewhat off this line but, as in the chromium plot (Fig.1), the $[\text{Fe}(\text{CN})_6]^{4-}$ species appears to fall on the main line.

We can expect to generate a series of such relationships for, in general, all metal redox couples (at least those involving the t_{2g} set in O_h) allowing for changes in spin state, stereochemistry and coordination number and also for water or organic solvent measurements.

In Figs.7-10 are shown data sets for a variety of other couples ranging from classical six coordinate coordination complexes of iron, chromium, ruthenium, rhodium, osmium, niobium and tantalum, to organometallic derivatives containing carbonyls, dinitrogen, phosphines, etc. Some five coordinate species are also included. There is no doubt that these plots are generally linear and that ligand additivity is amply demonstrated over a very wide range of complexes.

Correction for Isomers:-

Within the ruthenium data set, cis/trans, mer/fac isomers etc usually have essentially the same potential and indeed, for many such pairs of coordination complex isomers for other redox couples, there is little difference in potential, though there are certainly a few exceptions.

This is not generally true for organometallic species where such differences may be 0.1 - 0.5V. We follow here the method of Treichel and Bursten^{2,8} who developed a correction for the HOMO energy of a carbonyl complex in terms of the number of carbonyl π^* orbitals which interact with the HOMO. Thus for a $d^6 \text{M}(\text{CO})_6$ species, all three t_{2g} orbitals (degenerate HOMO) interact with 4 CO π^* orbitals. For a trans- $\text{ML}_4(\text{CO})_2$ species, the t_{2g} splits to place xy (HOMO) above xz, yz assuming that xy is now stabilised by 0 CO π^* and xz, yz is stabilised by 2 CO π^* interactions. In the case of cis- $\text{ML}_4(\text{CO})_2$ xz, yz (1 π^* interaction) lies above xy (2 π^* interactions). For the moment, we ignore the possible stabilisation of the d orbitals by non-carbonyl ligands. Since such stabilisation of the HOMO is proportional to the number of CO groups bonded thereto and the relevant potential is proportional to the HOMO energy^{3,8}, one may introduce a variable x such that for the carbonyl species under discussion, eqn.(8) is replaced by:-

$$E_{\text{obs}} = f[\Sigma E_L] + C + mx \quad (10)$$

where $m = 4, 0$ and 1 respectively for the hexacarbonyl, trans and cis dicarbonyl, with similar corrections for other isomeric species (shown in Table 3).

Isonitrile complexes frequently have higher potentials than those directly derived from eqn.(8). This suggests that isonitrile ligands also strongly influence the π^* bonding d orbitals. They may also be included in eqn.(10) by adding thereto the energy variable y modified by the number of isonitrile ligands, m' which interact directly with the HOMO orbital (eqn.(11)):-

$$E_{\text{obs}} = f[\Sigma E_L] + C + mx + m'y \quad (11)$$

Values for m and m' , for mixed carbonyl-isonitrile species are shown in Table 3.

First, Fig. 7 (upper) shows data for the Mn(II)/Mn(I) couple in a series of carbonyl derivatives following eqn. (3) and hence uncorrected for the specific isonitrile or for enhanced isonitrile bonding. Two linear correlations are evident, the isonitriles being badly scattered but the carbonyl being reasonably linear. A value for y , in eqn. (11) was derived from $[\text{Mn}(\text{CNR})_6]^{+}$: (for each R, $y(R)$)

$$y(R) = 1/4[\text{obs. potential} - \text{calc. potential using eqn. (11)}] (m=0, m' \approx 4). \quad (12)$$

Similarly, using the value of $y(\text{Me})$, an initial value of x (eqn. (11)) was derived by fitting the observed potential for $[\text{Mn}(\text{CO})_5(\text{CNR})]^{+}$ ($m=3, m' \approx 1$). These two values were then used in eqn. (11) to re-calculate all the manganese data according to Table 3. The fit was improved by allowing y to vary to a best fit (least squares) over all manganese complexes with given CNR, resulting in a final value of $y(R)$ slightly different from that calculated via eqn. (12). Energy variable x was also varied to a best fit over all the carbonyl complexes. The result is also shown in Fig. 7 (lower) where the improvement is dramatic. Importantly, the final line upon which all the complexes lie is essentially that of the carbonyl complexes in the uncorrected version shown in Fig. 7, within experimental error. Such corrections (eqn. (11)) add some complexity to the analysis. They can be ignored with the higher oxidation state species. Ignoring them with carbonyl, non-isonitrile data leads to some scatter but relatively accurate data can be obtained nevertheless. It would be prudent to include these corrections where isonitriles are concerned (vide infra). Values of x and y are shown in Table 3. Corrections have not been made for other ligands.

It is noteworthy that there is a reasonable linear correlation for these carbonyl derivatives and for the chromium and molybdenum species shown in Fig. 3. The scatter is somewhat larger than observed in the non-carbonyl chromium, iron and osmium data sets in part because of the lack of correction for specific (non-carbonyl) ligand interactions with the π -d electrons but probably mostly as a result of the synergistic interactions which take place within these species.

Incomplete Data Sets

When E_{L} values for all ligands in a complex are known, its calculated potential may be derived from the regression line where available (eqns. (4,8)). However, the method may also be used for generic series of complexes when the E_{L} value for a specific ligand is not available. Consider, for example, a set of complexes ML_4XY , for which $E_{\text{L}}(\text{L})$ is unavailable but $E_{\text{L}}(\text{X})$ and $E_{\text{L}}(\text{Y})$ are known. We require:-

$$\text{E}_{\text{obs}} = f[4 * E_{\text{L}}(\text{L}) + E_{\text{L}}(\text{X}) + E_{\text{L}}(\text{Y})] + C \quad (13)$$

An experimental slope and intercept may be derived from:-

$$\text{E}_{\text{obs}} = f'[E_{\text{L}}(\text{X}) + E_{\text{L}}(\text{Y})] + C' \quad (14)$$

However (13) may be rewritten:-

$$\text{E}_{\text{obs}} = f[E_{\text{L}}(\text{X}) + E_{\text{L}}(\text{Y})] + 4fE_{\text{L}}(\text{L}) + C \quad (15)$$

$$\text{Hence } f = f' \text{ and } C' = C + 4fE_{\text{L}}(\text{L}) \quad (16)$$

The key observation is that for a generic series of complexes with a constant f , as in this case ML_4 , the slope of the correlation will be the same as that calculated had the $E_{\text{L}}(\text{L})$ been known. Thus the slope is defined but the intercept is

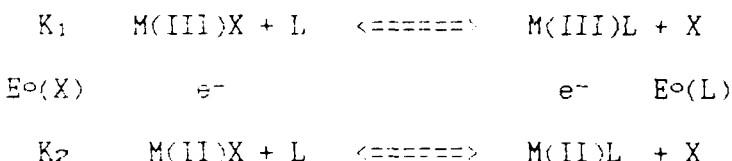
indeterminate. For a specific group of complexes of M, of given structure, a correlation line may already have been derived. If the generic set of complexes belong to the same structural type and if the slope is the same as that previously deduced, then one might conclude that these complexes must lie on the same line - hence C is known and $E_L(L)$ may be derived.

Consider, for example, the series of complexes $\text{Fe}(\text{OMG-BF}_2)\text{XY}$, ($\text{FeOMG-BF}_2 = \text{bis}[(\text{difluoroboryl})\text{dimethylglyoximate}]iron$)³¹ where a direct value for $E_L(\text{OMG-BF}_2)$ is unavailable. A plot of eqn.(14) yields a straight line of slope 1.06. These complexes (probably) belong to the same stereochemistry and spin state group as $[\text{Fe}(\text{bpy})_3]^{2+}$ and indeed display essentially the same slope. They are shown plotted in Fig.6 using a value of C which gives the best fit to this line. From this value of C, one may derive $E_L(\text{OMG-BF}_2) = 0.22V$.

While it is obvious that the $E_L(L)$ value for an unknown ligand could be derived by fitting its electrochemical datum to a correlation line, one may, in general, not know which correlation line to use, leading to ambiguity in the $E_L(L)$ value. The key proposition here is that one may study a group of related complexes all containing the same unknown core ligand, and use the resulting slope to infer the correct correlation line and hence spin state and stereochemistry.

Significance of Slope and Intercept

Slope:- The potential of a given redox couple reflects the relative binding strength of the two oxidation states to the ligand concerned, the more positive the potential, the more strongly binding being the lower oxidation state. This is clearly seen in the free energy correlation shown in the following simplified scheme:-



where:-

$$E^\ominus(\text{L}) - E^\ominus(\text{X}) = (RT/nF)\ln(K_2/K_1)$$

A slope of unity for correlation of a specific $M(n)/M(n-1)$ couple with $[E_L]$ indicates that the binding of $M(n)$ to a set of ligands, relative to $M(n-1)$ is the same as for the $\text{Ru(III)}/\text{Ru(II)}$ couple. A slope exceeding unity shows a greater sensitivity of the metal core towards the ligand, i.e. a greater degree of polarisation by the ligand or, in other words, stabilisation of the lower oxidation state is increasingly favoured with increasing E_L , relative to Ru(II) .

It is surprising how many slopes are close to unity though this may possibly be fortuitous given the relatively small number of data sets which have been processed to date, and the fact that all but one involve the t_{2g} (in O_h) orbitals. It is also surprising that both π -acids and π -donors tend to fall on the same line, for given structural type, even though one expects them to bind in differing relative degrees to the lower and higher oxidation states.

There are few data sets yet available for different oxidation states of the same metal ion. Nevertheless one can expect that the slope will vary with the couple involved if only because of the changing degree of σ and π -bonding which will occur. For example a low spin d^5/d^6 couple where the lower oxidation state species is stabilised by π -acids through back donation should yield a different slope (greater than the corresponding d^4/d^5 where the extent of π -back donation in the d^5 ion would be greatly reduced relative to that in the d^6 ion). In the case of niobium where

π -bonding is not likely significant. both the Nb(V)/Nb(IV) and Nb(IV)/Nb(III) couples have the same slope. However many more data are clearly necessary before this can usefully be discussed.

Intercept:- The value of the intercept C is determined by a number of contributions. Thus the potential might be written:-

$$E_{\text{obs}} = a + nb + c + f[\Sigma \text{L}] \quad (17)$$

where **a** (always positive) is defined as the M(n)/M(n-1) ionisation energy in the gas phase. The variable **b** (always negative) may then be defined in a fashion identical to the spherical electrostatic term in ligand field theory raising all the energy levels by the same degree determined by **n**, the number of ligands and arising from the electrostatic repulsion between ligand lone pair and metal d electrons. Variable **c** (either sign) then depends upon the reference electrode and upon the difference in solvation energies of M(n) and M(n-1); thus $C = a+nb+c$.

The sum $a+nb+c$ is defined as zero for a basis set of ruthenium complexes in acetonitrile, versus NHE. Since essentially all six coordinate Ru(III)/(II) couples, in acetonitrile, fall on the same line and given that charge appears not to be an important factor (**c** is constant) we might conclude that **b** is a constant for that set of complexes and therefore, for a given oxidation state, does not significantly depend upon the nature of the ligand. The discrimination of the ligand is then all contained within $[\Sigma \text{L}]$ and provides the linearity which would not otherwise be observed, i.e. if **b** did vary significantly with ligand, a linear plot would not be observed (unless the variation itself is a linear function of some property of the ligand). The value of **b** will vary with different metals and vary with different oxidation states of the same metal. The variation in **a**, with oxidation couple, makes a major contribution to the magnitude of the intercept, especially to the larger negative values derived for low oxidation state couples.

Further Comments on Charge Effects and Solvation

Charge effects will reveal themselves in comparisons of aqueous with organic solvent data. While the Ru(III)/Ru(II) couple for net charge (2+) species in water has roughly the same slope (1.14) as that (defined as unity) in organic solvent, that of the Os(III)/Os(II) couple in water is 1.61 for the net charge (2+) species. Unfortunately there are insufficient data to define the slopes for other net charge species. However the marked variation in the osmium slope for organic to aqueous solvent does reveal that the redox dependence on solvent is not confined to the intercept; the slope is also influenced by the solvent. It is true that both the ruthenium and osmium water data sets presented here are dominated by polyammine species (see Appendix) which may interact with water in a different fashion from species such as $[\text{M}(\text{terpy})_3]^{2+}$. Nevertheless the ammine and non-ammine complexes do appear to lie on essentially the same line; if the ammine complexes of ruthenium or osmium are considered alone the slope increases only slightly (1.28 for ruthenium, 1.76 for osmium). This may not be significant given the scatter in the water data.

That the slope in water is higher, is an intriguing new observation likely due to several factors including a modification of the M-L bond by outer sphere solute-solvent interactions and by entropy changes due to modifications in solvent structure by the charged species.^{27,28}

It is surely significant that, in Fig.5, the $[\text{Fe}(\text{II})\text{L}_6]^{2+}$ type species lie on the same line as the $[\text{Fe}(\text{CN})_6]^{4-}$ species. Both the solvation enthalpy (from equation) and solvation entropy are functions of charge squared.²⁷ Species having the same difference in solvation free energy for the M(n) and M(n-1) redox levels, would make the same contribution to **c** and lie on the same line; this is seen to be

the case here since $(3+)^2 - (2+)^2 = (3-)^2 - (2-)^2$.

Other Coordination Numbers:-

One can anticipate that a set of six coordinate species, which for example, lose a ligand upon reduction to form five coordinate species, will generate a separate correlation line from those where ligand loss does not occur. Following eqn.(8), the Ru(III)/Ru(II) potential for a q coordinate RuL_q species, in acetonitrile, might be written:-

$$E_{obs}(RuL_q) = a + qb + c + qE_L \quad (18)$$

If we suppose that the numerical magnitudes of **a,b,c** are approximately the same as for the six coordinate species (**a** will be identical) and recall that for a six coordinate ruthenium species (Ru(III)/Ru(II)) $a + b + c = 0$, then it follows that:-

$$E_{obs}(RuL_q) = qE_L - (6-q)b \quad (19)$$

Thus the E_L values derived from six coordinate species cannot be directly used, with eqn.(8), for other coordination numbers since they have effectively been modified by a contribution from the spherical term. However since **b** is assumed roughly constant for all ligands for a given redox process, we can expect other coordination numbers still to yield straight line correlations with ΣE_L following eqn. (8). The intercept will contain the term $-(6-q)b$ (which is positive) and the potential will be more positive than for the corresponding ML₆ species. In principle this provides a useful method to evaluate **b**; straight line correlations are indeed observed with the M(III)/M(II) couple in Fe(TPP)X, Fe(OEP)X and Mn(TPP)X (Table 2) Fig.10).

The Electrochemical Series of Ligands.

The existence of this additivity provides a ligand sequence which is directly analogous to the spectrochemical series of D_q in that all ligands behave relatively the same way towards all metal ions. This sequence may be abbreviated into ranges which however certainly overlap and should be regarded only as a guide to estimate the E_L values of ligands which do not appear in Table 1.

E_L -.63 ----> 0 (V)

OH⁻, most Xⁿ⁻ ions, including S anions, strong π-bases.

E_L 0 -----> 0.1 (V)

Saturated amines falling into a fairly narrow range, weakly π-acid unsaturated amines.

E_L 0.1 -----> 0.40 (V)

Unsaturated amines of stronger π-acid character, pyridines, bipyridines etc.

E_L 0.30 -----> 0.40 (V)

Hard thioethers, nitriles, softer phosphines.

E_L 0.35 -----> 0.50 (V)

Isonitriles, harder phosphines, arsine, stibines, softer phosphites.

E_L 0.50 -----> 0.65 (V)

harder phosphites.

E_L 0.65 ----> 0.75 (V)

Dinitrogen, nitrites.

E_L 0.70 ----> 0.95 (V)

Positively charged ligands, π -acid olefins.

E_L 0.9 (V)

CO (0.99 most positive member)

The relative E_L values reflect availability of charge for donation to the metal ion and have little connection with the spectroscopic Dq values where, for example, cyanide and carbon monoxide are close together in Dq value. Indeed being derived from the Ru(III)/Ru(II) t_{2g}^5/t_{2g}^6 couple, it is not surprising that they fall in a sequence largely determined by their π -bonding or π -anti-bonding behaviour.

Less Well-Behaved Systems - CNR, NO, Water, DMSO, Hydride and Macroyclic Complexes.

The considerable extent to which ligand additivity provides a viable means to estimate redox potentials would seem to "throw away" a lot of chemistry and reduce redox behaviour to the summation of a series of non-interacting M-L fragments. Indeed for a wide range of ligands and metal redox couples this appears to be roughly true despite variation of π -acid or π -basic character in both metal and ligand. This is an unexpected result which does not appear to have been previously recognised. Solvation phenomena also appear only to play a small role in determining redox energies provided that specific solvent-solute interactions are absent. Those complexes which do not fit their apparent correlation line should be considered in some depth. If one can exclude trivial explanations such as important coupled preceding or following chemical reactions, then the failure may arise for cogent chemical bonding reasons.

Carbonyl species generally fit rather well even where the specific isomer corrections are ignored. Inclusions of these isomer corrections show stabilisations of the order of 0.1 - 0.15 eV per CO-d orbital interaction. However it is likely that the $E_L(CO)$ value itself actually contains within it some stabilisation effect and should, in fact, be a little smaller if used with a metal ion in which there is no π back-bonding if such is possible. Thus the value may be a little inflated explaining why it falls off the PPLC correlation (Fig.2).

Isonitriles are a very special case which deserve more comment. Considering CNMe, an $E_L(CNMe)$ value of 0.55V is derived from $[Ru(bpy)_2(CNMe)_2]^{2+}$ ³². However isonitrile E_L values derived from correlation with the Pickett/Pletcher ligand parameters yield values around 0.4 (Appendix). A similar but smaller, distinction is seen with the carbonyl ligand. The best fit for the manganese isonitrile data shown in Fig.7, was obtained by assuming a value of ca. 0.37V for each CNMe plus a correction of 0.19V for each CNMe bound to the HOMO orbital (isomer correction). The ligand CNPh required a larger correction, 0.31V (Table 3). Other metal isonitrile species were fitted in a similar manner. It is particularly relevant that the trivalent and non-backdonating d³ $[Cr(CNR)_6]^{3+}$ species could be fitted with the lower $E_L(CNR)$ values (ca 0.37) without a correction for the number of π -bonding isonitrile groups, while the low spin d⁶ $[Fe(CNMe)_6]^{2+}$ ³³ and related species did require such correction (ca 0.10 (V)/ π -bonding CNMe (Table 3)), as did $[Ru(CNMe)_6]^{2+}$ which shows no Ru(III)/Ru(II) redox process below 3.2V (vs NHE)³³ (and therefore requires a large correction). The validity of this approach is inferred from the excellent regression fits obtained from a large body of data.

The variation in $E_L(CNR)$ may be related to the fact that the isonitrile group may be linear or bent.³⁴⁻³⁶ The linear isonitrile parallels carbonyl in its stinging. The bent isonitrile will occur in situations where there is extensive back donation.

The latter case may be exemplified by mixing of both $M(O)(CNR)$ and $M(I)(CNR(1-))$, as might be inferred from the PES data for $[Ku(bpy)_2(CNR)_2]^{2+}$ species in the Ru(III) region.³⁷ Note that valence bond contributions of the CNR(1-) canonical form will shift positively all metal d orbitals, not just the HOMO. Indeed Pombeiro, Pickett and Richards¹⁴ had previously noted the variation in the PPLC parameter for isonitriles in various complexes and suggested that bent isonitriles should have a E_L value (eqn.2) approximately 0.3 volts larger than a linear isonitrile. X-ray structural data show significant variations in bond angles for coordinated isonitrile groups; thus the actual correction may vary from one set of complexes to another.

It does not seem necessary to use this rather more complex fitting procedure for any other ligand yet studied.

A value for the macrocycle TPP can be derived from ruthenium data (Table 1). This corresponds to a six coordinate metal-in-the-plane species. Using this number the six coordinate $L_2Fe(II)(TPP)$ species lie close to their correlation line for $(LS)Fe(III)/(LS)Fe(II)$ (Fig.6) (they apparently have the same slope) and a slight adjustment for $E_L(TPP)$ due to the relative sizes of Ru(II) and Fe(II) and the fixed macrocycle hole size, would place them on the line. However the corresponding $L_2Cr(II)(TPP)$ species (spin state of $L_2Cr(II)TPP$ is unknown) lie off both the low spin and high spin octahedral Cr(II) correlation lines (Fig.4) perhaps for reasons of hole size, or possibly because the correct correlation line has not been identified. The slope for the $L_2Cr(TPP)$ data is relatively low (Table 2) indicating that the Cr(III)-L bond does not significantly favour Cr(III) over Cr(II) in the TPP environment.

The nitrosyl ligand offers especial interest since the contribution depends upon the amount of charge transferred thereto and hence upon the metal core; it will be discussed elsewhere.³⁸ Water, as a ligand, yields a somewhat variable E_L value near 0 in the range -0.05 -- +0.1. The contribution of water likely depends upon how dry an organic solvent is and whether there are any hydrogen bonding species around. In water the $E_L(H_2O)$ value will depend critically upon pH. In coordinating organic solvents the water molecule may be partially or wholly solvolysed, adding a complicating factor. DMSO is poorly behaved yielding a variety of E_L values spanning ca 0.4 - 0.55. This may be a consequence of variable S or O coordinate binding. The hydride ion usually gives rise to irreversible redox processes but its E_L value may be estimated to lie near -0.5; the PPLC value of -0.3V is likely somewhat low.

Summary: The availability of E_L parameters allows one to:-

- a) predict the redox potential of a given metal couple when its structural and spin state information are available. For example, in a complex voltammogram this will aid in redox couple assignment;
- b) predict the structure and spin state for a metal complex based upon fitting its observed redox potential to a previous correlation;
- c) allow one to calculate the thermodynamic value for a redox couple when kinetic effects or coupled chemical reactions, etc, prevent it from being experimentally derived;
- d) design a metal complex to have a specific redox potential. With further development, correlations with other properties such as infrared stretching frequencies, photoelectron binding energies, certain rate constants,^{8,39,40-42} charge transfer transition energies^{19,24,43,44} etc can be included. Thus molecules having a range of characteristics can be designed using a procedure based upon E_L values;
- e) provide bonding (synergism, non-innocence etc) or structural information where a predicted value disagrees significantly with the experimental value;
- f) provide a means of designing metal complexes with specific excited state redox potentials, through analysis involving ground state electrochemical predicted energies and excited state transition energies;

g) provide a means of evaluating solvation energies, especially aquation energies;
h) through detailed understanding of the slopes and intercepts, provide additional insight in to the nature of the metal-ligand bond.

To learn exactly how general is this approach requires considerable further data evaluation especially with data sets involving σ^* redox orbitals. Readers with extensive electrochemical data sets are invited to advise the author for inclusion in future EL studies.

Acknowledgement

The author is indebted to the Natural Sciences and Engineering Research Council (NSERC, Ottawa) and the Office of Naval Research (Washington) for financial assistance.

Table 1 E_L Parameter Values, vs NHE

Ligands	E _L	Ref. ^a
1,10-Phenanthroline(1,10) {16}	0.26	[23]
1,10-Phenanthroline, 2,9-Dimethyl (2,9-diMe2phen)	0.20	[23]
1,10-Phenanthroline, 4,7-dimethyl (4,7-diMe2phen)	0.23	[23]
1,10-Phenanthroline-5,6-dicne (phendione)	0.28	[45]
1,1,1,5,5,5-hexafluoro-2,4-pentanedionato (hfac) (1-)	0.17	[46]
1,1,1,-trifluoro-2,4-pentanedionato (tfac) (1-)	0.03	[46]
1,1-bis(Diphenylarsino)methane (PDA)	0.35	[23]
1,1-bis(Diphenylphosphino)methane (dppm)	0.43	[47]
1,2-bis(Dimethylphosphino)ethane	0.28	PPLC, [12]
1,2-bis(Dimethylphosphino)benzene (Diphos)	0.31	[48]
1,2-bis(Dimethylarsino)benzene	0.30	[48]
1,2-bis(Diphenylarsino)benzene (diars)	0.34	[23]
1,2-bis(Diphenylphosphino)benzene (ophenPPh ₂)	0.45	(Os), [44]
1,2-bis(Diphenylarsino)ethane (Ph ₂ AsCCAsPh ₂)	0.44	(Os), [44]
1,2-bis(Diphenylphosphino)acetylene (ADP)	0.46	[23]
1,2-bis(Diphenylphosphino)ethane (Ph ₂ PCCPPh ₂) (dppe)	0.36	[23]
1,2-bis(Diphenylphosphino)ethene-cis (Ph ₂ PC=CFPh ₂)	0.49	[47]
1,2-bis(Diphenylphosphino)propane (PDP)	0.42	[47]
1,2-bis(Ethylthio)ethane	0.32	[47]
1,2-bis(Methylthio)ethane	0.33	[47]
1,2-bis(Phenylthio)ethane	0.36	[47]
1,2-Diamino-2-methyl-propane	0.11	[23]
1-(2-Pyridyl)-3,5-dimethylpyrazole (Pydipy)	0.23	[23]
1,2,4,-Triazole,(2,3,5-tri-2'-pyridyl)	0.29	[23]
1,3-Diphenyl-1,3-propanedionato (1-) (dbmo)	-0.04	[46]
1,4,5,8-Tetrazaphenanthrene	0.36	[23]
1-Phenyl-1,3-butanedionato (1-) (bzac)	-0.06	[46]
1-Phenyl-4,4,4,-trifluoro-2,4-pentanedionato (bztfo) (1-)	0.05	[46]
1,2-bis(4-pyridyl)ethane (BPA)	0.26	[23]
2,2'-Bipyridine {94}	0.259	[23]
2,2,6,6,-tetramethyl-3,5-heptanedionato (dpmo) (1-)	-0.13	[46]
2,2 -Bipyrazine {6} (bpz)	0.36	[23]
2,2'-BipyrazineH (1+)	0.75	[23]
2,2-Bipyridine, 4,4'-dibromo (4,4-Br ₂ bpy)	0.28	[23]
2,2-Bipyridine, 4,4-dimethyl (4,4-Me ₂ bpy)	0.23	[23]
2,2-Bipyridine, 4,4-diphenyl	0.23	[23]
2,2-Bipyridine, 4-methyl,4-vinyl	0.23	[23]
2,2-Bipyridine, 4-nitro	0.30	[23]
2,2-Bipyridine, 5,5-dimethyl (5,5-Me ₂ bpy)	0.23	[23]
2-(2-pyridyl)quinoline (PQ)	0.25	[23]
2,4-pentanedionato (1-) (acac)	-0.08	[23,46,48]
2-methylthioquinoline	0.30	[47]
3,3'-biisoquinoline (biqu)	0.24	[23]
3,4-bis(Methylthio)toluene	0.38	[47]
2,6,9,thithiaundecane	0.34	[50]
3-amino-1-propene	0.13	[23]
3-bromo-2,4-pentanedionato (1-) (3-Bracac)	-0.03	[51]
3-chloro-2,4-pentanedionato (1-) (3-Clacac)	-0.03	[51]
3-iodo-2,4-pentanedionato (1-) (3-Iacac)	-0.03	[51]
3-methyl-2,4-pentanedionato (1-) (3-Meacac)	-0.11	[51]
3-phenyl-2,4-pentanedionato (1-) (3-Phacac)	-0.09	[51]

4-cyanopyridine-Ru(NH ₃) ₅ (2+)	0.33	[52]
4-methoxyphenylcyanide	0.60	[23]
4,4'-Bipyridine (4,4bpy)	0.27	[23]
4,4'-bithiazole (btz)	0.20	[23]
8-hydroxyquinolinato (1-)	-0.09	[53]
8-methylthioquinoline	0.30	[23]
Acetonitrile {18}	0.34	[23]
Acrylonitrile (ECN)	0.38	[23]
Ammonia	0.07	[23, 27]
Azide (1-)	-0.30	[23]
Benzohydroximato, p-methoxy (2-)	-0.54	[54]
Benzohydroximato, p-nitro (2-)	-0.50	[54]
Benzohydroximato, (2-)	-0.52	[54]
Benzoisonitrile	0.41	[23]
Benzoisonitrile, 2,6-dichloro	0.46	PPLC
Benzoisonitrile, p-chloro	0.38	PPLC
Benzoisonitrile, p-methoxy	0.36	PPLC, [37]
Benzoisonitrile, p-methyl	0.37	PPLC
Benzylamine (PMA)	0.14	[23]
Benzylisonitrile	0.56	[37]
Binaphthyridine (binapy) (#)	0.27	[55]
Bipyridazine	0.30	[23]
Bipyrimidine	0.31	[23]
Bipyrimidine(4,4-Me ₂)	0.24	[23]
Biquinoline (biq) {17}	0.29	[55, 56]
Bis(4-pyridyl)acetylene	0.27	[23]
Bis-alkyl-1,3-diazabutadiene	0.13	(CrCO), [57]
Bi-benzimidazolato (1-)	-0.03	[58]
Bi-benzimidazolato (2-)	-0.18	[58]
Bi-benzimidazole (BiBizim)	0.17	[58]
Bi-imidazole (BiimHz)	0.13	[58]
Bromide (1-) {5}	-0.22	[23]
Butane(n) thiolate (1-)	-0.55	[59]
Butylamine (BA)	0.13	[23]
Butyronitrile (PRC)	0.35	[23]
Carbon monoxide (CO)	0.99	[23]
Chloride (1-) {45}	-0.24	[23]
Cyanate (1-)	-0.25	PPLC
Cyclam ([14]aneN ₄)	0.10	(Ag), [60]
Cyanide (1-) {6}	0.02	[23, 61]
Cyclohexylisonitrile	0.32	PPLC
Diethyldithiocarbamato (1-)	-0.08	[23, 62]
Diethylsulphide {6}	0.35	[47]
Dimethyldithiocarbamato (1-)	-0.12	[23]
Dimethylglyoximate (1-)	0.01	[53]
Dimethyl Dimercaptomaleato (2-)	-0.47	[59]
Dimethylphenylphosphine (MMP)	0.34	[23]
Dimethylphosphine	0.34	PPLC
Dimethylsulfide	0.31	[47]
Dimethylsulphide	0.32	[47]
Dimethylsulphoxide (DMSO {8}) (#)	0.47	[47, 50, 63]
Dinitrogen	0.66	PELC
Di-2-pyridyl ketone (dpk) (#)	0.28	[64]
Di-2-pyridylaminato (1-) (#)	-0.16	[65]
Di-2-pyridylamine	0.18	[65]

Ethanethiolate (1-)	-0.56	[59]
Ethyl nitrite	0.70	[23]
Ethylene	0.76	(Aq), [66]
Ethylenediamine	0.06	[23, 27]
Ethylnitrile {4}	0.33	[23]
Ethylxanthato (1-)	-0.02	[23]
Fluoride (1-)	-0.42	(CrO ₄), [57]
Formate (1-) (For)	-0.30	[23]
Glycine (1-) (glyc)	-0.05	[23]
Hydride (1-)	-0.30	PPLC
Hydroxide (1-)	-0.59	PPLC
Imidazole	0.12	[23]
Imidazole, 4-vinyl	0.14	[23]
Imidazole, N-methyl (Melm)	0.08	[23]
Iodide (1-)	-0.24	[23]
Isonicotinamide (isna)	0.26	(Aq), [68]
isonitrosopropiophenonato (1-)	0.01	[23]
i-Propyl nitrite	0.68	[23]
i-Propylamine	0.05	[23]
i-Propylisonitrile	0.36	PPLC
Maleonitriledithiolate (2-) (mnt)	-0.33	[59]
Methyl nitrite	0.72	[23]
Methyldiphenylphosphine (MPP)	0.37	[23]
Methylisonitrile	0.37	PPLC
Methylphenylsulphide	0.33	[47]
Naphthyridine	0.24	[23]
Nitrate (1-) {8}	-0.11	[23]
Nitrite (1-)	0.02	[23]
Nitrosonium (1+) (NO) {8} (#)	-0.52	[23]
Norbornadiene	0.46	[23]
n-Butylisonitrile	0.48	[68]
N-butylsalicylaldiminato (1-)	0.46	[70]
N-MethylBenzohydroximato, p-methyl (1-)	-0.22	[54]]
N-MethylBenzohydroximato, p-nitro (1-)	-0.18	[54]]
N-methylpyrazinium (NMePyz) (1+)	0.73	(Os), [26, 68,
N-methylpyridinium, 4-cyano (1+) (#)	-0.17	[52]
N-methyl-(2-pyridyl)-imine (pymi)	0.27	[23]
Octaethylporphyrin (OEP)_ (2-) (metal in plane)	-0.07	[71]
Oxalate (2-)	-0.17	[23]
o-Acetylphenolate (1-)	-0.07	[70]
o-Propionylphenolate (1-)	-0.10	[70]
Pentafluorothiolato (1-)	-0.33	[23]
Ferchlorate (1-)	0.06	[23]
Phenol, 2-benzimidazolato (1-)	-0.20	[58]
Phenol, 2-benzimidazolato (2-)	-0.35	[58]
Phenylcyanide	0.37	[23]
Phenylcyanide, 3-cyano	0.43	(Aq), [72]
Phenylcyanide, 4-chloro	0.40	(Aq), [72]
Phenylcyanide, 4-cyano	0.49	(Aq), [72]
Phenylcyanide, 4-methoxy	0.38	(Aq), [72]
Phenylcyanide, 4-methyl	0.37	(Aq), [72]
Polyvinylimidazole	0.11	[23]
Pyridazine (pyd)	0.32	[23, 68]
Pyrazine (pyz) (5)	0.33	[23]
Pyrazine, 1,3-(di-2-pyridyl) (dpypyd) (#)	0.32	[23, 72, 74]

Pyrazole	0.23	[23]
Pyrazole (1-)	-0.24	[23]
Pyridine {24}	0.25	[23]
Pyridine, 2-aminoethyl	0.17	[23]
Pyridine, 2-aminomethyl	0.13	[23]
Pyridine, 2-benzimidazolato (1-)	-0.08	[58]
Pyridine, 2-benzimidazolyl	0.20	[58]
Pyridine, 2-imidazolyl	0.18	[58]
Pyridine, 2-isouinolyl	0.26	[23]
Pyridine, 2-Phenylazo (AzPy)	0.49	[23]
Pyridine, 2-quinolyl	0.25	[23]
Pyridine, 2-tolylazo (MeAzPy)	0.41	[23]
Pyridine, 2-(2'-naphthyridine)	0.22	[23]
Pyridine, 3,5-dichloro	0.35	(Aq), [72]
Pyridine, 3,5-dimethyl	0.21	(Aq), [72]
Pyridine, 3-aminoethyl	0.11	[23]
Pyridine, 3-carboxamido	0.36	(Aq), [72]
Pyridine, 3-iodo	0.29	[23]
Pyridine, 4-acetyl	0.30	[23]
Pyridine, 4-aldehydo	0.31	(Aq), [72]
Pyridine, 4-carboxamido	0.28	(Aq), [72]
Pyridine, 4-carboxylic acid	0.29	(Aq), [72]
Pyridine, 4-Chloro	0.26	(Aq), [72]
Pyridine, 4-cyano	0.32	[52]
Pyridine, 4-cyano (nitrile bonded)	0.38	[52]
Pyridine, 4-methyl (4-pic)	0.23	[23]
Pyridine, 4-Phenyl	0.23	(Os), [52]
Pyridine, 4-styryl	0.23	[23]
Pyridine, 4-trifluoromethyl	0.31	(Aq), [72]
Pyridine, 4-t-butyl	0.23	[23]
Pyridine, 4-vinyl (6)	0.20	[23]
Pyridine, poly(4-vinyl) (PVP)	0.23	[23]
Pyrimidine (pyrim)	0.29	[23]
Pyrimidine,H (1+)	0.43	[23]
Pyrroliidinecarboxyldithionato (1-)	-0.12	[23]
p-Chlorothiophenolate (1-)	-0.43	[58]
p-Methylthiophenolate (1-)	-0.48	[58]
p-Toluenethiolate (1-)	-0.48	[58]
p-Toluol-sulfonate (1-)	-0.13	[23]
Salicylaldehyde (1-)	-0.04	[70]
Selenocyanate (1-)	-0.23	[75]
Dipyrido[3,2-c:2',3'-e]pyridazine (Taphen)	0.37	[23]
Terpyridine {16}	0.25	[23]
Tetrahydrothiophene	0.30	[50]
Tetr phenylporphyrin (TPP) (2-) (metal in-plane)	0.00	[71]
Tetraaza macrocycle (TZ) ²⁻	0.14	[63]
Thiocyanato (1-)	-0.06	[23]
Thiophencolate (1-)	-0.53	[23]
Thiourea	-0.13	[23]
Triazole,1,2,4	0.18	[23]
Triazole,1,2,4 3,5-bis(pyridin-2-yl) (1-)	0.05	[76]
Triazole,1,2,4 3,5-bis pyridin-2-yl)H	0.11	[76]
Triazole,1,2,4 4-allyl	0.12	[23]
Triazole,1,2,4 4-methyl	0.11	[23]
Triazole,1,2,4 4-phenyl	0.14	[23]

Triazole, 1,2,4 (1-)	-0.17	[23]
Triethylphosphine	0.04	[42,56]
Trifluoroacetate (1-) (TFA)	-0.15	[23]
Trifluorosulfonate (1-)	0.16	(Osm., [7])
Trimethylphosphine	0.33	(Osm., [6,7])
Trimethylphosphite	0.43	[64]
Triphenylarsine	0.38	[23]
Triphenylphosphine (10)	0.39	[23]
Triphenylphosphite	0.58	PPLC
Triphenylstibine	0.58	[23]
Tritolylyphosphine (MeP)	0.37	[33]
Tri-n-Butylphosphine	0.29	[56]
Tri-n-propylphosphine	0.34	[56]
t-1,2-diaminocyclohexane	0.39	[23]
t-1,2-bis(4-pyridyl)ethene (BPE)	0.26	[23]
t-Butylisocyanide	0.36	PPLC
t-butylthioclate (1-)	-0.55	[53]
Vinyl imidazole	0.13	[23]
Water (diss.)	0.04	[42,78]

Footnotes: a) The number in round brackets is the net charge on the ligand; the letter code in round brackets is the abbreviation used in the Appendix and in ref.[23]; Most data were derived from potentials observed with 1-8 compounds - numbers in braces show where more than 3 compounds were used and the data averaged. The (#) sign means that the Si datum is somewhat variable from one complex to another.
 b) (Osm.), (CrCl), (Aq) mean that the data were derived from osmium, chromium carbonyl or aqueous ruthenium ammine data as referenced, respectively, assuming a perfect fit to the appropriate correlation expression. PPLC Signifies derived by fitting to the WinNet V.1.1 tether ligand parameter, at TM = 2, 7, 12, 17-tetramethyl-1,6,11,16-tetraazaporphyrinogen. 63

Table 2 Slope and Intercept Data^a, Volts vs NHE

		Slope /SD ^d	Intercept /SD ^d	Regress. ^b	# ^c	Solvent
Chromium	Cr(III)/Cr(II)(LS)	1.18/0.06	-1.72/0.15	0.98	18	Organic
Chromium	Cr(III)/Cr(II)(LS)	0.575/0.04	-1.12/0.05	0.98	8	Water
Chromium	Cr(III)/Cr(II)(HS)	0.84/0.05	-1.18/0.09	0.98	14	Organic
Chromium	Cr(I)/Cr(0) ^e	0.52/0.02	-1.75/0.1-	0.97	39	Organic
Iron	Fe(III)/Fe(II)(LS)	0.68/0.02	0.24/0.04	0.99	24	Water
Iron	Fe(III)/Fe(II)(LS) ^e	1.10/0.05	-0.43/0.12	0.99	14	Organic
Iron	Fe(III)/Fe(II)(HS)	0.89/0.04	-0.25/0.04	0.99	8	Organic
Iron	Fe(III)/Fe(II){5CN} ^f	1.60/0.14	****g	0.99	5	Organic
Iron	Fe(III)/Fe(II){5CN} ^h	1.61/0.12	****g	0.99	5	Organic
Manganese	Mn(III)/Mn(II){5CN}	0.38/0.12 ^f	****g	0.85	6	Organic
Manganese	Mn(II)/Mn(I) ^e	0.81/0.02	-1.76/0.08	0.99	23	Organic
Molybdenum	Mo(I)/Mo(0)	0.74/0.03	-2.25/0.10	0.99	24	Organic
Niobium	Nb(V)/Nb(IV)	0.76/0.02	1.24/0.02	0.999	3	Organic
Niobium	Nb(IV)/Nb(III)	0.75/0.01	-0.12/0.01	0.999	3	Organic
Osmium	Os(III)/Os(II)	1.01/0.02	-0.40/0.11	0.98	80	Organic
Osmium	Os(III)/Os(II)	1.61/0.05	-1.30/0.11	0.99	18	Water
Rhenium	Re(IV)/Re(III)	0.85/0.05	0.50/0.13	0.98	18	Organic
Ruthenium	Ru(III)/Ru(II)	1.14/0.04	-0.35/0.09	0.97	44	Water
Tantalum	Ta(V)/Ta(IV)	0.85/0.03	0.67/0.03	0.998	3	Organic
Pickett/Pletcher		1.17/0.05	-0.86/0.04	0.98	18	
Ruthenium	Ru(III)/Ru(II) XYZ	0.97/0.01	0.04/0.03	0.99	103	Organic

a) All six coordinate except where noted. b) Correlation coefficient.

c) Number of data points. d) Standard error in volts. e) See Table 3 for isomer f) Tetraphenylporphyrin - metal out of plane. g) indeterminate intercept due to use of a macrocycle core of uncertain E_L value. h) from Octaethylporphyrin, metal out of plane. 5CN = five coordinate, LS = low spin, HS = high spin.

Table 3 Contributions to the HOMO Orbital energies in Isonitrile and Carbonyl Derivatives^a

M(CNR) _x (CO) _y	n(CO)	M(CNR) _x (CO) _y
M(CNR) ₆	0	4
M(CNR)sc(CO)	1	3
c-M(CNR) ₄ (CO) ₂	2	2
t-M(CNR) ₄ (CO) ₂	2	2
m-M(CNR) ₃ (Cl) ₃	2	1
f-M(CNR) ₃ (CO) ₃	2	2
e-M(CNR) ₂ (CO) ₄	3	1
t-M(CNR) ₂ (CO) ₄	4	0
M(CNR)(CO) ₅	3	1
M(CO) ₆	4	0

^a) Corrections for M(CNR)_x(CO)_y in columns 1,2 assuming that the isonitrile ligand stabilises the d orbitals to a greater degree than carbon monoxide. Corrections for ML_x(CO)_y in column 3 assuming no interaction by ligand L.

NB: HOMO Corrections for data in Table 2 (see text for significance): Cr(I)/Cr(II) PhNC, 0.19, MeNC, 0.19, CO, 0.15V. Mn(II)/Mn(I) - PhNC, 0.31, MeNC, 0.19, CO, 0.15V. Mo(IV)/Mo(III) - no corrections applied. Fe(III)/Fe(II) - MeNC, 0.10V.

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Appendix A

Data presented in Figs.

All data referenced to NHE. Charges refer to that of the reduced species in the couple, though in many cases, the electrochemical observation may have been carried out on the bulk oxidised species. The regression lines listed in Table 2, do not necessarily include all the points on a given Figure; outlying points have been omitted in some cases.

References Fig.1	Complex Data in Organic Solvent	Obs	Calc.	ΣE_L
		Ruthenium(III)/Ruthenium(II) (open circles)		
[23]	Ru(bpy) ₂ (CH ₃ CN)NO (3+)	0.8	0.87	0.86
[23]	Ru(bpy) ₂ (CH ₃ CN)NO ₂ (1+)	1.41	1.39	1.40
[23]	Ru(bpy) ₂ (CH ₃ CN)NO ₃ (1+)	1.26	1.26	1.27
[23]	Ru(bpy) ₂ (Py)Na (1+)	0.82	0.84	0.83
[23]	Ru(bpy) ₂ (Py)NO ₂ (1+)	1.3	1.30	1.31
[23]	Ru(bpy) ₂ (Py)NO ₃ (1+)	1.167	1.18	1.18
[23]	Ru(bpy) ₂ (4-t-BuPy)NO ₃ (1+)	1.12	1.15	1.15
[23]	Ru(bpy) ₂ (4-vinylPy)NO ₂ (1+)	1.275	1.26	1.26
[23]	Ru(bpy) ₂ (4-vinylPy)NO ₃ (1+)	1.15	1.13	1.13
[23]	Ru(bpy) ₂ (Cl)NO ₂	0.81	0.83	0.81
[23]	Ru(bpy) ₂ (Cl)NO ₃	0.69	0.70	0.68
[23]	Ru(bpy) ₂ (Py)CH ₃ CN (2+)	1.6	1.61	1.63
[23]	Ru(bpy) ₂ (Py)CN (1+)	1.28	1.30	1.31
[23]	Ru(bpy) ₂ (Py)Cl (1+)	1.019	1.05	1.04
[23]	Ru(bpy) ₂ (Py)TFA (1+)	1.13	1.14	1.14
[23]	Ru(bpy) ₂ (4-AcPy)Cl (1+)	1.06	1.09	1.09
[23]	Ru(bpy) ₂ (4-vinylPy)CH ₃ CN (2+)	1.53	1.57	1.58
[23]	Ru(bpy) ₂ (4-vinylPy)Cl (1+)	1	1.00	1.00
[23]	Ru(bpy) ₂ (PyrimH)Cl (2+)	1.21	1.21	1.21
[23]	Ru(bpy) ₂ (Pyr)Cl (1+)	1.12	1.12	1.12
[23]	Ru(bpy) ₂ (Pyr)NO ₂ (3+)	1.38	1.38	1.38
[23]	Ru(bpy) ₂ (BPA)Cl (1+)	1.01	1.05	1.05
[23]	Ru(bpy) ₂ (BPE)Cl (1+)	1.02	1.06	1.05
[23]	Ru(bpy) ₂ (MPP)Cl (1+)	1.15	1.165	1.16
[23]	Ru(bpy) ₂ (MeP)Cl (1+)	1.18	1.16	1.16
[23]	Ru(bpy) ₂ (PDP)Cl (1+)	1.15	1.21	1.21
[23]	Ru(bpy) ₂ (PPh ₃)NO ₂ (1+)	1.49	1.43	1.43
[23]	Ru(bpy) ₂ (PPh ₃)NO ₃ (1+)	1.31	1.30	1.30
[45]	Ru(bpy)(phen)dione ₂ (2+)	1.67	1.64	1.65
[47]	c-Ru(bpy) ₂ (Ph ₂ MeP)Cl (1+)	1.15	1.165	1.16
[47]	c-Ru(bpy) ₂ (Ph ₃ P)Cl (1+)	1.18	1.17	1.17
[23]	Ru(bpy)(Terpy)(CH ₃ CN) (2+)	1.55	1.60	1.61
[23]	Ru(bpy)(Terpy)(NH ₃) (2+)	1.41	1.35	1.36
[61]	Ru(bpy)(terpy)(CN) (1+)	1.3	1.285	1.29
[79]	Ru(bpy)(biq)(4,4-Me ₂ bpy) (2+)	1.54	1.536	1.54
[78]	Ru(bpy)(biq)(phen) (2+)	1.59	1.57	1.58
[79]	Ru(bpy)(biq)(pq) (2+)	1.63	1.57	1.58
[79]	Ru(bpy)(biq)(i-biq) (2+)	1.53	1.55	1.56
[79]	Ru(bpy)(biq)(BiimH ₂) (2+)	1.33	1.34	1.35
[79]	Ru(bpy)(biq)(bipyrim) (2+)	1.7	1.69	1.71
[79]	Ru(bpy)(biq)(binapy) (2+)	1.51	1.48	1.49
[52]	Ru(bpy)(biq)Cl ₂	0.7	0.62	0.60
[80]	Ru(bpz) ₂ (CH ₃ CN)Cl (1+)	1.56	1.54	1.55
[80]	Ru(bpz) ₂ Cl ₂	1.04	0.98	0.97

[81]	Ru(bpz) ₂ Br ₂	1.03	1.03	1.02
[81]	Ru(bpz) ₂ (NO ₂) ₂	1.42	1.43	1.44
[23]	Ru(phen) ₂ (CH ₃ CN) ₂ (2+)	1.685	1.69	1.71
[23]	Ru(phen) ₂ CN ₂	1.122	1.07	1.07
[23]	Ru(phen) ₂ (Py) ₂ (2+)	1.515	1.52	1.53
[23]	Ru(phen) ₂ (4-vinylPy) ₂ (2+)	1.49	1.48	1.49
[23]	Ru(phen) ₂ (Pyz)Cl (1+)	1.1	1.12	1.11
[23]	Ru(phen) ₂ (naphthyridine) (2+)	1.51	1.50	1.51
[82]	Ru(phen) ₂ (Py) ₂ (2+)	1.515	1.52	1.53
[82]	Ru(phen) ₂ (en) (2+)	1.125	1.19	1.19
[82]	Ru(phen) ₂ (Py)Cl (1+)	1.045	1.04	1.04
[82]	Ru(phen) ₂ (acac) (1+)	0.875	0.88	0.87
[82]	Ru(phen) ₂ (ox)	0.725	0.71	0.70
[82]	Ru(phen) ₂ Cl ₂	0.573	0.56	0.54
[23]	Ru(4,7-diMe ₂ phen) ₂ (Pyz)Cl (1+)	1.01	1.04	1.03
[23]	Ru(terpy)(BPE) ₃ (2+)	1.47	1.51	1.52
[83]	Ru(terpy)(Py) ₃ (2+)	1.5	1.485	1.49
[83]	Ru(terpy)(CH ₃ CN) ₃ (2+)	1.73	1.75	1.76
[83]	c-Ru(terpy)(CH ₃ CN) ₂ Cl (1+)	1.17	1.18	1.18
[83]	t-Ru(terpy)(Py) ₂ Cl (1+)	1.07	1.01	1.00
[83]	Ru(terpy)(Py) ₂ (CH ₃ CN) (2+)	1.53	1.57	1.58
[83]	Ru(terpy)(Py)(CH ₃ CN)Cl (1+)	1.09	1.085	1.09
[83]	Ru(terpy)(Py)(PF ₃ Ph) ₂ Cl (1+)	1.1	1.14	1.14
[23]	Ru(pydipy) ₂ (CH ₃ CN) ₂ (2+)	1.6	1.55	1.56
[23]	Ru(AzPy) ₂ Br ₂	1.19	1.21	1.21
[23]	Ru(AzPy) ₂ Cl ₂	1.205	1.16	1.16
[23]	Ru(MeAzPy) ₂ Br ₂	1.137	1.21	1.21
[23]	Ru(MeAzPy) ₂ Cl ₂	1.147	1.16	1.16
[63]	Ru(TZ)(CH ₃ CN) ₂	1.29	1.24	1.24
[63]	Ru(TZ)(Py) ₂	1.05	1.06	1.06
[63]	Ru(TZ)(Py)(CH ₃ CN)	1.16	1.15	1.15
[63]	Ru(TZ)(4,4-bpy) ₂	1.08	1.07	1.07
[56]	Ru(biq) ₂ Cl ₂	0.72	0.69	0.68
[56]	Ru(biq) ₂ (PEt ₃)H ₂ O (2+)	1.48	1.47	1.48
[61]	Ru(biq) ₂ (CN) ₂	1.17	1.20	1.20
[84]	m-Ru(Py) ₃ Cl ₃	0.08	0.06	0.02
[50]	RuBr ₂ (SMe ₂) ₃ (DMSO)	1.055	1.06	1.055
[50]	RuBr ₂ (SEt ₂) ₃ (DMSO)	1.035	1.045	1.04
[50]	RuBr ₂ (SEt ₂) ₂ (DMSO) ₂	0.985	1.00	0.99
[50]	RuCl ₂ (SMe ₂) ₄	0.805	0.81	0.8
[50]	RuCl ₂ (SEt ₂) ₃ (DMSO)	1.045	1.055	1.05
[50]	RuCl ₂ (SMe ₂) ₂ (DMSO) ₂	0.945	0.96	0.95
[61]	Ru(DMCH) ₂ (CN) ₂	1.04	1.08	1.08
[61]	Ru(i-biq) ₂ (CN) ₂	1.01	0.99	0.98
[85]	Ru(terpy)(dppyz)Cl (1+)	1.18	1.14	1.14
[23]	Ru(AzPy) ₂ (N ₃) ₂ check	1.2	1.045	1.04
[23]	Ru(bpy) ₂ (CH ₃ CN)Cl (1+)	1.08	1.14	1.13
[23]	Ru(bpy) ₂ (NH ₃)(NO ₂) (1+)	1.08	1.15	1.15
[23]	Ru(bpy) ₂ (NH ₃)(NO ₂) (1+)	0.94	1.02	1.02
[83]	t-Ru(terpy)(4-Pic) ₂ Cl (1+)	1.02	1.01	1.00
[83]	Ru(terpy)(4-Pic) ₃ (2+)	1.47	1.46	1.46
[86]	Ru(terpy)(Py) ₂ (4-Pic) (2+)	1.47	1.47	1.47
[56]	Ru(tpy)(biq)(PMe ₃)Cl (1+)	1.2	1.18	1.18
[56]	Ru(bpy)(biq)(PEt ₃)Cl (1+)	1.19	1.18	1.18
[86]	Ru(bpy)(biq)(P(n-Pr) ₃)Cl (1+)	1.2	1.19	1.19

[56]	Ru(bpy)(biq)(P(n-Bu) ₃)Cl (1+)	1.2	1.19	1.19
[56]	Ru(bpy)(biq)(PPh ₃)Cl (1+)	1.26	1.22	1.22

Fig. 1 Data in Water

Ruthenium(III)/Ruthenium(II)

[28]	Ru(en) ₃ (2+)	0.18	0.10	0.39
[72]	Ru(NH ₃) ₆	0.05	0.135	0.42
[72]	Ru(NH ₃) ₅ Pyz (2+)	0.49	0.43	0.68
[72]	Ru(NH ₃) ₅ Py (2+)	0.3	0.34	0.6
[72]	Ru(NH ₃) ₅ (4-AcPy) (2+)	0.39	0.44	0.685
[72]	Ru(NH ₃) ₅ (CH ₃ CN) (2+)	0.43	0.44	0.69
[72]	Ru(NH ₃) ₅ (PhCN) (2+)	0.485	0.48	0.72
[72]	c-Ru(NH ₃) ₄ (PhCN) ₂ (2+)	0.37	0.82	1.02
[68]	Ru(NH ₃) ₅ (pyrim) (2+)	0.44	0.44	0.69
[68]	Ru(NH ₃) ₅ (4,4-bpy) (2+)	0.33	0.35	0.61
[86]	t-Ru(NH ₃) ₄ (4-Pic)(Py) (2+)	0.45	0.52	0.76
[86]	t-Ru(NH ₃) ₄ (4-Pic)(pyz) (2+)	0.61	0.61	0.84
[86]	t-Ru(NH ₃) ₄ (4-Pic)(4-AcPy) (2+)	0.52	0.62	0.845
[86]	t-Ru(NH ₃) ₄ (Py) ₂ (2+)	0.48	0.55	0.78
[86]	c-Ru(NH ₃) ₄ (Py) ₂ (2+)	0.505	0.55	0.78
[86]	t-Ru(NH ₃) ₄ (Py)(4-AcPy) (2+)	0.55	0.64	0.865
[86]	t-Ru(NH ₃) ₄ (Py)(pyz) (2+)	0.65	0.64	0.86
[86]	t-Ru(NH ₃) ₄ (4-AcPy) ₂ (2+)	0.60	0.74	0.95
[86]	t-Ru(NH ₃) ₄ (pyz)(4-AcPy) (2+)	0.74	0.73	0.94
[86]	t-Ru(NH ₃) ₄ (pyz) ₂ (2+)	0.78	0.72	0.93
[86]	c-Ru(NH ₃) ₄ (pyz) ₂ (2+)	0.86	0.72	0.93
[86]	c-Ru(NH ₃) ₄ (bpy) (2+)	0.51	0.56	0.79
[87]	Ru(NH ₃) ₅ (4-CNPy) (2+)	0.57	0.50	0.74
[78]	Ru(NH ₃) ₄ (P-nBu ₃) ₂ (2+)	0.71	0.64	0.86
[80]	Ru(en) ₂ (bpy) (2+)	0.59	0.54	0.78
[80]	Ru(en) ₂ (phen) (2+)	0.55	0.54	0.77
[80]	Ru(cyclam)(Py) ₂ (2+)	0.57	0.68	0.90
[80]	Ru(cyclam)(bpy) (2+)	0.65	0.70	0.92
[80]	Ru(cyclam)(phen) (2+)	0.63	0.70	0.91
[88]	c-Ru(NH ₃) ₄ (Py) ₂ (2+)	0.505	0.55	0.78
[73,88]	t-Ru(NH ₃) ₄ (Py) ₂ (2+)	0.49	0.55	0.78
[73]	Ru(NH ₃) ₄ (dpypyz) (2+)	0.82	0.695	0.91
[23]	Ru(bpy) ₃ (2+)	1.51	1.40	1.53
[23]	Ru(bpy) ₂ (PMA) (2+)	1.21	1.16	1.32
[23]	Ru(bpy) ₂ (4-vinylPy) ₂ (2+)	1.285	1.30	1.44
[23]	Ru(bpy) ₂ (PVP)(CH ₃ CN) (2+)	1.48	1.49	1.61
[23]	Ru(bpy) ₂ (PVP)Cl (1+)	1	0.83	1.02
[23]	Ru(4,4-diMe ₂ bpy) ₃ (2+)	1.09	1.25	1.40
[23]	Ru(bpz) ₃ (2+)	2.22	2.125	2.16
[23]	Ru(bpyim)(NH ₃) ₄ (2+)	0.756	0.68	0.81
[23]	Ru(pn-n) ₃ (2+)	1.28	1.42	1.54
[89]	Ru(phen) ₂ (en) (2+)	1.04	0.97	1.15
[89]	Ru(phen)(en) ₂ (2+)	0.79	0.54	0.77
[89]	Ru(terpy) ₂ (2+)	1.25	1.36	1.49
[28]	Ru(NH ₃).5Cl (1+)	-0.04	-0.22	0.11
[28]	Ru(NH ₃) ₅ (NCS) (1+)	0.105	0.01	0.285
[28]	Ru(NH ₃) ₅ Br (1+)	-0.21	-0.18	0.13

Fig.2

	Obs.	Calc.	ΣE_L NHE
CO	0	0.295	0.99
PhPh ₃	-0.35	-0.41	0.39
CF ₃ CO ₂ ⁻	-0.78	-1.04	-0.15
CN ⁻	-1.0	-0.84	0.02
PhCN	-0.4	-0.43	0.37
Phenazopy	-0.37	-0.38	0.41
bpz	-0.45	-0.44	0.36
bipyrimid	-0.5	-0.50	0.31
bpy	-0.55	-0.56	0.26
MeCN	-0.58	-0.47	0.34
Py	-0.59	-0.57	0.25
bisPhimidaz	-0.645	-0.665	0.17
CF ₃ PhAcAc ⁻	-0.765	-0.80	0.05
NH ₃	-0.77	-0.76	0.09
en	-0.79	-0.77	0.08
Ph ₂ AcAc ⁻	-0.865	-0.92	-0.04
NCS ⁻	-0.88	-0.93	-0.055
MePhAcAc ⁻	-0.89	-0.935	-0.06
AcAc ⁻	-0.91	-0.96	-0.08
Br ⁻	-1.17	-1.12	-0.22
Cl ⁻	-1.19	-1.15	-0.24
azide ⁻	-1.26	-1.22	-0.3

Fig.3 Data in Organic Solvent

Osmium(III)/Osmium(II)

	Obs	Calc.	ΣE_L
[44,82] Os(phen) ₂ Cl ₂	0.24	0.14	0.54
[90] Os(bpy) ₂ Br ₂	0.28	0.20	0.60
[24] Os(bpy) ₂ (ox)	0.345	0.31	0.71
[82] Os(phen) ₂ (ox)	0.39	0.30	0.70
[48] Os(diphos) ₂ Cl ₂	0.45	0.36	0.76
[48] Os(diphos) ₂ Br ₂	0.39	0.32	0.72
[82] Os(phen) ₂ (acac) (1+)	0.48	0.47	0.87
[24,44,82] Os(bpy) ₂ (acac) (1+)	0.495	0.48	0.88
[44] Os(bpy) ₂ (4,4bpy)Cl (1+)	0.56	0.62	1.02
[82] Os(phen) ₂ (en) (2+)	0.57	0.76	1.16
[82] Os(phen) ₂ (Py)Cl (1+)	0.58	0.64	1.04
[44] Os(bpy) ₂ (Py)Cl (1+)	0.59	0.65	1.04
[44] Os(bpy) ₂ (Py)Br (1+)	0.59	0.67	1.07
[44] Os(bpy) ₂ (CH ₃ CN)Cl (1+)	0.65	0.74	1.13
[90] Os(bpy) ₂ (pyz)Cl (1+)	0.67	0.72	1.12
[82] Os(bpy) ₂ (glyc) (1+)	0.675	0.54	0.94
[82,90] Os(bpy) ₂ (CN)Cl	0.695	0.68	1.08
[82,90] Os(bpy) ₂ (en)Cl (2+)	0.725	0.77	1.16
[44] Os(bpy) ₂ (Ph ₃ As)Cl (1+)	0.75	0.78	1.17
[44] m-Os(bpy) ₂ (PEt ₃) ₂ Cl (1+)	0.76	0.80	1.30
[44] Os(bpy) ₂ (Ph ₃ P)Cl (1+)	0.8	0.79	1.18
[26] Os(NH ₃) ₅ (N-MePz) (3+)	0.80	0.79	1.19
[44] m-Os(bpy) ₂ (PMes) ₂ Cl (1+)	0.84	0.87	1.27
[44] m-Os(bpy) ₂ (PPhMe ₂) ₂ Cl (1+)	0.89	0.885	1.28
[82] Os(4,4'-Me ₂ bpy) ₂ (2+)	0.895	0.95	1.34
[91] Os(bpy) ₂ (BiBicimH ₂) (2+)	0.9	0.98	1.38

[44]	Os(phen)Py ₄ (2+)	0.96	1.12	1.52
[44]	m-Os(bpy)(PPh ₂ Me) ₃ Cl (1+)	0.99	0.99	1.39
[44]	Os(bpy) ₂ (Py) ₂ (2+)	0.98	1.14	1.54
[44,82]	Os(phen) ₂ (Py) ₂ (2+)	0.985	1.13	1.53
[77]	Os(phen)(dppy)(PhMe ₂ P)Cl (2+)	1.04	1.18	1.58
[82]	Cs(phen) ₃ (2+)	1.05	1.15	1.54
[44]	Os(bpy) ₂ (4,4-Mezopy) ₂ (2+)	1.05	1.09	1.48
[82]	Os(bpy) ₃ (2+)	1.06	1.16	1.55
[44]	Os(bpy) ₂ (pyz)(Py) (2+)	1.08	1.22	1.61
[44]	Os(phen) ₂ (CH ₃ CN) ₂ (2+)	1.11	1.315	1.71
[92]	Os(bpy) ₂ (CH ₃ CN) ₂ (2+)	1.15	1.32	1.72
[88]	Os(5-Cl-Phen) ₃ (3+)	1.15	1.17	1.56
[45]	Os(phen) ₂ (phendione) (2+)	1.17	1.26	1.65
[44]	Os(bpy) ₂ (pyz) ₂ (2+)	1.21	1.30	1.69
[44]	Os(bpy) ₂ (Ph ₃ P)(NO ₂) (1+)	1.21	1.27	1.665
[45]	Os(bpy) ₂ (phendione) (2+)	1.25	1.21	1.60
[44]	m-Os(bpy)(PPhMe ₂) ₃ (NO ₂) (1+)	1.29	1.37	1.76
[44]	Os(bpy) ₂ (Ph ₂ MeP)(CH ₃ CN) (2+)	1.29	1.34	1.74
[44]	Os(pnen) ₂ (Me ₂ PhP) ₂	1.33	1.305	1.70
[44]	t-Os(bpy) ₂ (Ph ₂ MeP) ₂ (2+)	1.34	1.38	1.78
[44]	Os(phen) ₂ (diars) (2+)	1.35	1.305	1.70
[44]	Os(bpy) ₂ (diars) (2+)	1.35	1.31	1.71
[77]	Os(bpy) ₂ (CO)(O ₂ CH) (1+)	1.37	1.34	1.73
[77]	Os(phen) ₂ (CO)Cl (1+)	1.38	1.38	1.78
[77]	Os(bpy) ₂ (CO)Cl (1+)	1.42	1.39	1.78
[44]	c-Os(bpy) ₂ (Ph ₂ MeP) ₂ (2+)	1.45	1.38	1.78
[94]	Os(bpy) ₂ (MeAzPy) (2+)	1.47	1.45	1.84
[77]	t-Os(phen)(Me ₂ P) ₂ (CO)Cl (1+)	1.49	1.53	1.83
[77]	Os(bpy) ₂ (CO)(O ₂ CCF ₃) (1+)	1.5	1.49	1.89
[44]	Os(bpy) ₂ (dppm) (2+)	1.51	1.49	1.89
[77]	t-Os(phen)(PhMe ₂ P) ₂ (CO)Cl (1+)	1.52	1.54	1.93
[44]	Os(bpy) ₂ (dppe) (2+)	1.54	1.52	1.92
[44]	Os(phen) ₂ (dppe) (2+)	1.54	1.52	1.91
[44]	Os(phen) ₂ (dppm)	1.56	1.49	1.88
[47]	Os(bpy) ₂ (dppy) (2+)	1.64	1.615	2.01
[44]	Os(phen) ₂ (dppy) (2+)	1.6	1.61	2.00
[77]	t-Os(phen)(Ph ₂ MeP) ₂ (CO)Cl (1+)	1.65	1.61	2.00
[44]	Os(bpy) ₂ (CNMe) ₂ (2+)	1.68	1.38	1.78
[44]	Os(bpy)(diars) ₂ (2+)	1.7	1.47	1.86
[44]	Os(phen)(diars) ₂ (2+)	1.71	1.46	1.85
[77]	t-Os(phen)(Ph ₃ P) ₂ (CO)Cl (1+)	1.74	1.65	2.04
[95]	Os(tpz) ₃ (2+)	1.76	1.77	2.16
[44]	Os(bpy) ₂ (CO)(NO ₂) (1+)	1.78	1.88	2.265
[77]	Os(phen)(dppy)(CO)Cl (1+)	1.78	1.84	2.23
[94]	Os(bpy)(MeAzPy) ₂ (2+)	1.88	1.76	2.15
[77]	Os(bpy) ₂ (CO)(Py) (2+)	1.91	1.89	2.28
[44]	Os(bpy)(dppm) ₂ (2+)	1.96	1.83	2.22
[77]	Os(bpy) ₂ (CO)(CH ₃ CN) (2+)	2.04	1.98	2.37
[44]	Os(bpy)(dppy) ₂ (2+)	2.05	2.07	2.46
[44]	Os(phen)(dppy) ₂ (2+)	2.08	2.07	2.45
[77]	Os(bpy) ₂ (CO)PPh ₃ (2+)	2.22	2.03	2.42
[95]	Os(dtz) ₃ (1-)	-0.36	-1.13	-0.72
[94]	Os(MeAzPy) ₃ (2+)	2.11	2.01	2.40
[47]	f-Os(bpy)(PMe ₂ Ph)Cl ₃	-0.31	-0.28	0.13
[48]	Os(bpy) ₂ Cl(tBuNH ₂)	0.52	0.54	0.94

[44] Os(bpy)₂(CNCH₂Ph)₂ (2+) 1.74 1.77 2.16

Fig.3 Data in Water

	Osmium(III)/Osmium(II)		
[99] Os(NH ₃) ₅ Cl (1+)	-0.86	-1.12	0.11
[99] Os(NH ₃) ₅ Br (1+)	-0.79	-1.12	0.11
[68] Os(NH ₃) ₅ Py (2+)	-0.395	-0.33	0.6
[68] Os(NH ₃) ₅ Pyz (2+)	-0.09	-0.21	0.68
[68] Os(NH ₃) ₅ Pyd (2+)	-0.21	-0.22	0.67
[68] Os(NH ₃) ₅ (4,4-bipy) (2+)	-0.22	-0.30	0.62
[68] Os(NH ₃) ₆ (2+)	-0.78	-0.82	0.42
[68] Os(NH ₃) ₅ (isma) (2+)	-0.24	-0.32	0.61
[100] Os(NH ₃) ₅ N ₂ (2+)	0.58	0.36	1.03
[66] Os(NH ₃) ₅ (CH ₃ CN) (2+)	-0.29	-0.19	0.63
[66] Os(NH ₃) ₅ (EtCN) (2+)	-0.35	-0.19	0.69
[66] Os(NH ₃) ₅ (ECN) (2+)	-0.17	-0.13	0.72
[66] Os(NH ₃) ₅ (PhCN) (2+)	-0.19	-0.16	0.71
[100] Os(NH ₃) ₅ CO (2+)	0.92	0.885	1.34
[68] Os(NH ₃) ₅ Pyrim (2+)	-0.26	-0.36	0.58
[101] Os(phen) ₂ (dppm) (2+)	1.57	1.59	1.79
[101] Os(phen) ₂ (dppy) (2+)	1.65	1.70	1.86
[101] Os(phen) ₃ (2+)	1.08	1.19	1.54
[101] Os(terpy) ₃ (2+)	1.23	1.10	1.49
[101] Os(phen) ₂ CO(Cl) (1+)	1.51	1.57	1.78

Fig.4 Data in Organic solvent

	Chromium(III)/Chromium(II)		
	Low spin Cr(II)		
[102] Cr(CNPh) ₆ (2+)	0.85	0.87	2.22
[102] Cr(CNPh,4-OMe) ₆ (2+)	0.75	0.73	2.10
[102] Cr(CNPh,4-Me) ₆ (3+)	0.83	0.86	2.16
[103] Cr(CNPh,4-Cl) ₆ (3+)	0.90	0.87	2.22
[103] Cr(AzPy) ₃ (2+)	1.30	1.16	2.46
[104] Cr(AzPy) ₂ Cl ₂	-0.19	-0.38	1.16
[104] Cr(bpy) ₂ (CN) ₂	-0.50	-0.47	1.08
[27] Cr(phen)(CN) ₄ (2-)	-0.98	-1.04	0.59
[105] Cr(bpy) ₃ (2+)	0.09	0.09	1.55
[105] Cr(phen) ₃ (2+)	-0.04	0.08	1.54
[43] Cr(terpy) ₃ (2+)	0.09	0.01	1.49
[43] Cr(5,5-Me ₂ bpy) ₃ (2+)	-0.08	-0.10	1.39
[104] Cr(4,4-Me ₂ bpy) ₃ (2+)	-0.13	-0.16	1.34
[104] Cr(phen) ₂ (NH ₃) ₂ (2+)	-0.65	-0.37	1.17
[104] Cr(phen) ₂ (NCS) ₂	-0.78	-0.67	0.92
[57] Cr(bpy) ₂ (NCS) ₂	-0.78	-0.65	0.93
[106] Cr(CNCMe ₃) ₄ (t-Bu-DAB) (2+)	0.91	0.90	2.24
[48] Cr(diphos) ₂ Cl ₂	-0.45	-0.85	0.76

Macrocyclic species

[106,107] Cr(TPP)(Py) ₂	-0.49	-0.46	0.48
[107] Cr(TPP)(Py)Cl (1-)	-0.56	-0.67	-0.01
[106] Cr(TPP)(4-Pic)Cl (1-)	-0.49	-0.68	-0.03
[106] Cr(TPP)(4-CNPy) ₂	-0.35	-0.35	0.73
[106] Cr(TPP)(4-Pic) ₂	-0.52	-0.47	0.44
[106] Cr(TPP)(4-OAcPy) ₂	-0.45	-0.42	0.57
[108] Cr(TPP)(3,5-Cl ₂ Py) ₂	-0.30	-0.38	0.86
[108] Cr(TPP)(MeIm) ₂	-0.72	-0.60	0.14
[109] Cr(TPP)(MeIm)Cl (1-)	-0.96	-0.74	-0.18

Fig.4 Data in Organic Solvent

[109] Cr(bda) ₃	(1-)
[109] Cr(3-SCNacac) ₃	(1-)
[109] Cr(3-CNacac) ₃	(1-)
[109] Cr(3-NO ₂ acac) ₃	(1-)
[109] Cr(bctfac) ₃	(1-)
[109] Cr(dbmo) ₃	(1-)
[109] Cr(dpmo) ₃	(1-)
[109] Cr(bzac) ₃	(1-)
[109] Cr(tfac) ₃	(1-)
[109] Cr(3-Pracac) ₃	(1-)
[109] Cr(3-Clacac) ₃	(1-)
[109] Cr(acac) ₃	(1-)
[104] Cr(phen) ₂ (acac) ₂	(1+)
[104] Cr(bpy)(en) ₂	(2+)
[104] Cr(phen)(en) ₂	(2+)

Chromium(III)/Chromium(II)
High Spin Cr(II)

-1.44	-1.66	-0.57
-0.97	-1.14	0.05
-0.97	-1.06	0.14
-0.91	-1.03	0.18
-0.65	-0.64	0.65
-1.39	-1.40	-0.27
-1.91	-1.84	-0.79
-1.45	-1.37	-0.23
-0.82	-0.91	0.33
-1.34	-1.31	-0.16
-1.83	-1.82	-0.17
-1.70	-1.64	-0.54
-0.49	-0.47	0.85
-0.64	-0.55	0.76
-0.65	-0.54	0.77

Fig.5 Data in Water

[89] Cr(CN) ₆	(4-)
[43] Cr(bpy) ₃	(2+)
[104] Cr(phen) ₃	(2+)
[104] Cr(phen) ₂ (H ₂ O) ₂	(2+)
[104] Cr(bpy) ₂ (H ₂ O) ₂	(2+)
[43] Cr(terpy) ₃	(2+)
[43] Cr(4,4-Me ₂ bipy) ₃	(2+)
[102] Cr(5,5-diMe ₂ bipy) ₃	(2+)

Chromium(III)/Chromium(II)
Low spin Cr(II)

-1.04	-1.05	0.12
-0.23	-0.22	1.55
-0.26	-0.23	1.54
-0.50	-0.48	1.11
-0.48	-0.48	1.11
-0.17	-0.26	1.49
-0.42	-0.34	1.34
-0.30	-0.32	1.38

Fig.5 Data in Water

[73] Fe(CN) ₄ (dpypz)	(2-)
[89] Fe(Me ₂ bipy) ₃	(2+)
[89] Fe(5-NO ₂ phen) ₃	(2+)
[89] Fe(phen) ₃	(2+)
[89] Fe(terpy) ₂	(2+)
[88] Fe(CN) ₆	(4-)
[110] Fe(bpy)(CN) ₄	(2-)
[89] Fe(bpy) ₂ (CN) ₂	
[111] Fe(4,7-Me ₂ phen) ₃	(2+)
[43] Fe(bipy) ₃	(2+)
[43] Fe(5,5-DiMe ₂ bipy) ₃	(2+)
[43] Fe(4,4-DiMe ₂ bipy) ₃	(2+)
[112] Fe(CN) ₅ (4-OAcPy)	(3-)
[112] Fe(CN) ₅ (Pty)	(3-)
[112] Fe(CN) ₅ (4-VinPy)	(3-)
[112] Fe(CN) ₅ (4-CNPy)	(3-)
[113] Fe(CN) ₅ (Imid)	(3-)
[113] Fe(CN) ₅ (Pyr)	(3-)

Iron(III)/Iron(II)
Low spin Fe(II)/Fe(III)

0.69	0.79	0.80
1.18	1.16	1.34
1.49	1.415	1.72
1.3	1.29	1.54
1.17	1.26	1.49
0.36	0.33	0.12
0.56	0.65	0.60
1.02	0.98	1.08
1.18	1.17	1.36
1.29	1.30	1.55
1.21	1.19	1.39
1.13	1.18	1.38
0.525	0.51	0.395
0.48	0.48	0.35
0.44	0.45	0.34
0.555	0.53	0.43
0.36	0.39	0.22
0.56	0.54	0.43

[113]	Fe(CN) ₅ (Pyrazole) (3-)	0.44	0.45	0.30
[112]	Fe(CN) ₅ (4-MePy) (3-)	0.45	0.47	0.33
[112]	Fe(CN) ₅ (4-ClPy) (3-)	0.58	0.49	0.36
[112]	Fe(CN) ₅ (3-COH ₂ Py) (3-)	0.52	0.50	0.38
[112]	Fe(CN) ₅ (4-COH ₂ Py) (3-)	0.51	0.52	0.40
[112]	Fe(CN) ₅ (4-COOH ₂ Py) (3-)	0.505	0.52	0.41
[112]	Fe(CN) ₅ (4-CH ₂ Py) (3-)	0.51	0.54	0.43
[88]	Fe(Phen) ₂ (CN) ₂ (0)	0.46	0.87	1.07
[87]	Fe(CN) ₅ (N-MePyr) (2-)	0.79	0.38	0.84

Fig.5 Data in Organic SolventIron(III)/Iron(II)
Low spin Fe(II)/Fe(III)

[33]	Fe(CNMe) ₆ (2+)	2.64	2.46	2.74
[88]	Fe(phen) ₃ (2+)	1.41	1.29	1.56
[43]	Fe(5,5-DiMebipy) ₃ (2+)	1.16	1.09	1.38
[43]	Fe(4,4-DiMebipy) ₃ (2+)	1.11	1.09	1.38
[88]	Fe(CN) ₆ (4-)	-0.31	-0.29	0.12
[43]	Fe(bipy) ₃ (2+)	1.27	1.28	1.55
[45]	Fe(phen)dione) ₃ (2+)	1.6	1.42	1.68
[88]	Fe(bpy) ₂ (CN) ₂	0.71	0.76	1.08
[114]	Fe(tterpy) ₂ (2+)	1.33	1.23	1.49
[115]	Fe(dppe) ₂ (NCMe) ₂ (2+)	1.72	1.95	2.16
[33]	Fe(phen) ₂ (CNMe) ₂ (2+)	1.79	1.76	1.98
[83]	Fe(5-Cl-phen) ₃ (2+)	1.41	1.29	1.56
[48]	Fe(diphos) ₂ Cl ₂	0.3	0.41	0.76
[48]	Fe(diphos) ₂ Br ₂	0.33	0.45	0.60

Macroyclic species

[116]	Fe(DMG-BF ₂) ₂ CH ₃ CN/TMIC	1.455	1.32	1.59
[117]	Fe(DMG-BF ₂) ₂ CH ₃ N(Bu) ₂	1.315	1.32	1.59
[118]	Fe(DMG-BF ₂) ₂ CH ₃ N ₂	1.215	1.29	1.56
[115]	Fe(DMG-BF ₂) Py ₂	1.025	1.09	1.38
[115]	Fe(DMG-BF ₂) MeIm ₂	0.725	0.72	1.04
[117]	Fe(TPP)(4-CNPy) ₂	0.54	0.26	0.62
[117]	Fe(TPP)(4-OAcPy) ₂	0.42	0.21	0.57
[117]	Fe(TPP)Py ₂	0.3	0.11	0.48
[117]	Fe(TPP)(4-Pic) ₂	0.26	0.06	0.44
[117]	Fe(TPP)(Im) ₂	0.16	-0.18	0.22
[117]	Fe(TPP)(3,5-Cl ₂ Py) ₂	0.55	0.29	0.64
[118]	Fe(TPP)(CN) ₂ (2-)	-0.38	-0.39	0.64

Fig.6

High spin Fe(II)/Fe(III)

[119]	Fe(acac) ₃ (1-)	-0.68	-0.68	-0.48
[119]	Fe(bzac) ₃ (1-)	-0.61	-0.57	-0.37
[119]	Fe(tfae) ₃ (1-)	-0.02	-0.04	0.24
[119]	Fe(dpme) ₃ (1-)	-0.91	-0.96	-0.80
[119]	Fe(dbmo) ₃ (1-)	-0.55	-0.48	-0.29
[119]	Fe(bzfa) ₃ (1-)	0.32	0.33	0.31
[119]	Fe(ptma) ₃ (1-)	-0.10	-0.14	-0.16

Fig. 7

	Obs.	Cal.	ΣE_L^a	ΣE_L^b
Manganese(II)/Manganese(I)				
[120] Mn(CNPh)s (1+)	1.24	1.24	3.7	2.46
[120] Mn(PhNC)s(CO) (1+)	1.52	1.54	4.07	3.64
[120] t-Mn(PhNC)4(CO)2 (1+)	1.78	1.84	4.44	3.62
[120] e-Mn(PhNC)4(CO)2 (1+)	1.94	1.84	4.44	3.62
[120] m-Mn(PhNC)s(CO)s (1+)	2.22	2.14	4.81	4.2
[120] f-Mn(PhNC)s(CO)s (1+)	2.36	2.31	5.02	4.2
[120] o-Mn(PhNC)s(CO)4 (1+)	2.52	2.61	5.39	4.78
[3] Mn(CNMe)s (1+)	0.62	0.66	2.95	2.32
[3] Mn(CNMe)sCO (1+)	1.03	1.09	3.51	2.74
[3] e-Mn(CNMe)s(CO)4 (1+)	2.38	2.45	5.19	4.7
[3] Mn(CNMe)(CO)s (1+)	2.89	2.88	5.72	5.32
[7] f-Mn(CO)s(CNMe)s (1+)	2.14	2.02	4.66	4.08
[7] m-Mn(CO)s(CNMe)s (1+)	1.97	1.94	4.57	4.08
[7] t-Mn(CO)2(CNMe)4 (1+)	1.52	1.52	4.04	3.46
[7] o-Mn(CO)2(CNMe)4 (1+)	1.68	1.52	4.04	3.46
[121] Mn(CO)(dpm)2(NCMe) (1+)	0.69	0.68	3.01	3.01
[121] Mn(CO)(dpm)2(CNMe) (1+)	0.77	0.70	3.04	3.04
[121] Mn(CO)(dpm)2Br	0.24	0.23	2.45	2.45
[121] Mn(CO)2(dpm)2 (1+)	1.1	1.21	3.66	3.66
[121] Mn(CO)(dpm)2CN	0.31	0.42	2.69	2.69
[121] Mn(CO)(dpm)2NCS	0.33	0.36	2.615	2.615
[121] Mn(CO)(dpm)2(CNBut) (1+)	0.78	0.70	3.03	3.03
[100] Mn(CO)sBr	2.16	2.32	5.03	4.73
[4] Mn(CO)s (1+)	2.975	3.38	6.34	5.94

a) Including isomer corrections; b) excluding isomer corrections - see Table 3.

Fig. 8

	Chromium(I)/Chromium(0)		
	Obs.	Cal.	ΣE_L
[122] f-Cr(CH ₃ CN)s(CO)s	0.20	0.48	4.29
[122] t-Cr(CO)4(PPh ₃) ₂	0.89	0.87	5.04
[122] e-Cr(CO)4(MeCN) ₂	0.59	0.81	4.94
[100] Cr(CO)s	0.64	0.72	4.76
[100] Cr(CO)sPPh ₃	1.69	1.64	6.54
[100] Cr(CO)sPEt ₃	1.39	1.25	5.78
[100] Cr(CO)sPMes ₃	1.34	1.21	5.71
[100] Cr(CO)sNH ₃	1.42	1.22	5.73
[100] Cr(CO)sNCMe	0.95	1.09	5.47
[100] Cr(CO)sPy	1.29	1.23	5.74
[100] Cr(CO)s(CN) ₂	1.14	1.18	5.65
[100] t-Cr(CO)4(PPh ₃) ₂	0.88	0.85	5.01
[100] f-Cr(CO)s(PMe ₂ Ph) ₃	0.42	0.47	4.28
[100] m-Cr(CO)s(POMe) ₃ s	0.60	0.52	4.38
[100] f-Cr(CO)s(POMe) ₃ s	0.74	0.60	4.53
[100] t-Cr(CO)2(dppe) ₂	-0.13	0.05	3.46
[100] e-Cr(CO)2(dppe) ₂	0.26	0.35	3.46
[100] Cr(CO)s(CN) ₂	0.85	0.73	4.77
[100] Cr(CO)s(CN) ₂	1.04	0.84	5.00
[122] CrPy(Cl)s	1.085	1.18	5.65
[4] Cr(CO)s(NMe)	1.215	1.24	5.77
[4] Cr(CNPh)s	-0.08	-0.08	3.72
[4] Cr(CNPh)s(CN) ₂	0.74	-0.17	3.04

[6]	Cr(CNPh,4-OMe) ₆	-0.225	-0.23	2.92
[6]	Cr(CNPh,4-Me) ₆	-0.19	-0.20	2.98
[120]	Cr(CO) ₅ (CNPh)	1.33	1.40	6.08
[120]	Cr(CO)(CNPh) ₅	0.09	0.20	3.76
[120]	f-Cr(CO) ₃ (CNPh) ₃	0.80	0.78	4.38
[120]	c-Cr(CO) ₄ (CNPh) ₂	0.98	1.06	5.42
[57]	Cr(CO) ₃ a(CNMe) ₂ (t-Bu-DAB)	0.18	0.21	3.77
[67]	Cr(CO) ₃ Cl (1-)	0.875	0.93	5.18
[67]	Cr(CO) ₃ Br (1-)	0.915	0.94	5.18
[67]	Cr(CO) ₃ I (1-)	0.935	0.92	5.14

Fig.8 (Cont.)

Molybdenum(I)/Molybdenum(0)

[100]	Mo(CO) ₄ bipy	0.36	1.06	4.48
[100]	c-Mo(CO) ₄ (PBu ₃) ₂	1.14	1.10	4.54
[100]	c-Mo(CO) ₂ (dppe) ₂	0.22	0.28	3.42
[100]	t-Mo(CO)(NCPh)(dppe) ₂	-0.16	-0.18	2.8
[100]	t-Mo(CO)(CN)(dppe) ₂ (1-)	-0.59	-0.44	2.45
[100]	t-Mo(CO)(SCN)(dppe) ₂ (1-)	-0.5	-0.49	2.375
[100]	t-Mo(CO)(Na)(dppe) ₂ (1-)	-0.76	-0.67	2.13
[9]	t-Mo(CO)(NCMe)(dppe) ₂	-0.25	-0.17	2.81
[123]	t-Mo(N ₂) ₂ (PMePh ₂) ₄	-0.17	-0.09	2.92
[100]	Mo(N ₂) ₂ (4-pic)(PMePh ₂) ₃	-0.24	-0.19	2.78
[100]	Mo(N ₂) ₂ (NMeIm)(PMePh ₂) ₃	-0.41	-0.31	2.63
[11]	t-Mo(N ₂) ₂ (dppe) ₂	0.08	-0.12	2.88
[100]	t-Mo(N ₂)(PhCN)(dppe) ₂	-0.24	-0.38	2.53
[100]	t-Mo(N ₂)(MeCN)(dppe) ₂	-0.34	-0.40	2.5
[100]	t-Mo(N ₂)(SCN)(dppe) ₂ (1-)	-0.63	-0.69	2.105
[100]	t-Mo(N ₂)(N ₃)(dppe) ₂ (1-)	-0.95	-0.87	1.86
[9]	t-Mo(N ₂)(CN)(dppe) ₂ (1-)	-0.74	-0.61	2.22
[9]	t-Mo(N ₂)(NH ₃)(dppe) ₂	-0.49	-0.57	2.27
[124]	Mo(CO) ₄ (i-prDAB)	0.89	0.88	4.24
[124]	Mo(CO) ₄ (i-BuDAB)	0.9	0.88	4.24
[124]	Mo(CO) ₄ (i-CyDAB)	0.87	0.88	4.24
[124]	Mo(CO) ₃ (CNMe)(t-BuDAB)	0.51	0.42	3.62
[124]	Mo(CO) ₃ (CH ₃ CN)(T-BuDAB)	0.45	0.40	3.59
[124]	Mo(CO) ₂ (CNCMe ₃) ₂ (t-BuDAB)	-0.02	-0.05	2.98

Fig.9

Niobium(V)/Niobium(IV)

[125]	NbCl ₆ (2-)	0.14	0.13	-1.45
[125]	Nb(CH ₃ CN)Cl ₅ (1-)	0.56	0.58	-0.87
[125]	Nb(CH ₃ CN) ₂ Cl ₄	1.03	1.02	-0.29

Niobium(IV)/Niobium(III)

[125]	NbCl ₆ (2-)	-1.2	-1.205	-1.45
[125]	Nb(CH ₃ CN)Cl ₅ (1-)	-0.78	-0.77	-0.87
[125]	Nb(CH ₃ CN) ₂ Cl ₄	-0.33	-0.335	-0.29

Tantalum(V)/Tantalum(IV)

[125] TaCl ₆ (2-)	-0.55	-0.56	-1.45
[125] Ta(CH ₃ CN)Cl ₅ (1-)	-0.09	-0.07	-0.37
[125] c-Ta(CH ₃ CN) ₂ Cl ₄	0.44	0.43	-0.29

Fig.9 (Cont.)

Rhenium(IV)/Rhenium(III)

[126] ReCl ₆ (3-)	-0.58	-0.71	-1.44
[127] ReCl ₄ (PM ₂ Ph) ₂ (1-)	0.1	0.27	-0.28
[128] Re(NCS) ₃ (3-)	0.13	0.26	-0.36
[87] Re(bpy)Cl ₄ (1-)	0.2	0.13	-0.44
[129] c-Re(CH ₃ CN) ₂ Cl ₄ (1-)	0.24	0.27	-0.28
[87] f-Re(bpy)(PM ₂ Ph)Cl ₃	0.71	0.62	0.14
[87] f-Re(bpy)(PPh ₃)Cl ₃	0.8	0.66	0.19
[127] ReCl ₃ (PM ₂ Ph) ₃	0.875	0.76	0.3
[87] m-Re(PPh ₃) ₂ (CH ₃ CN)Cl ₃	0.9	0.84	0.4
[87] m-Re(PMe ₂ Ph) ₃ Cl ₃	0.9	0.755	0.3
[130] Re(NCS) ₃ (PEt ₂ Ph)(bpy)	0.92	1.07	0.68
[130] Re(NCS) ₃ (PEt ₂ Ph)(bpy)	0.92	1.08	0.68
[130] Re(NCS) ₃ (PEt ₂ Ph)(dppe)	1.08	1.28	0.92
[87] t,c-Re(bpy)(PM ₂ Ph) ₂ Cl ₂ (1+)	1.12	1.11	0.72
[131] Re(dppe) ₂ Br ₂ (1+)	1.71	1.79	1.52
[131] Re(dppe) ₂ Cl ₂ (1+)	1.75	1.75	1.48

Fig.10

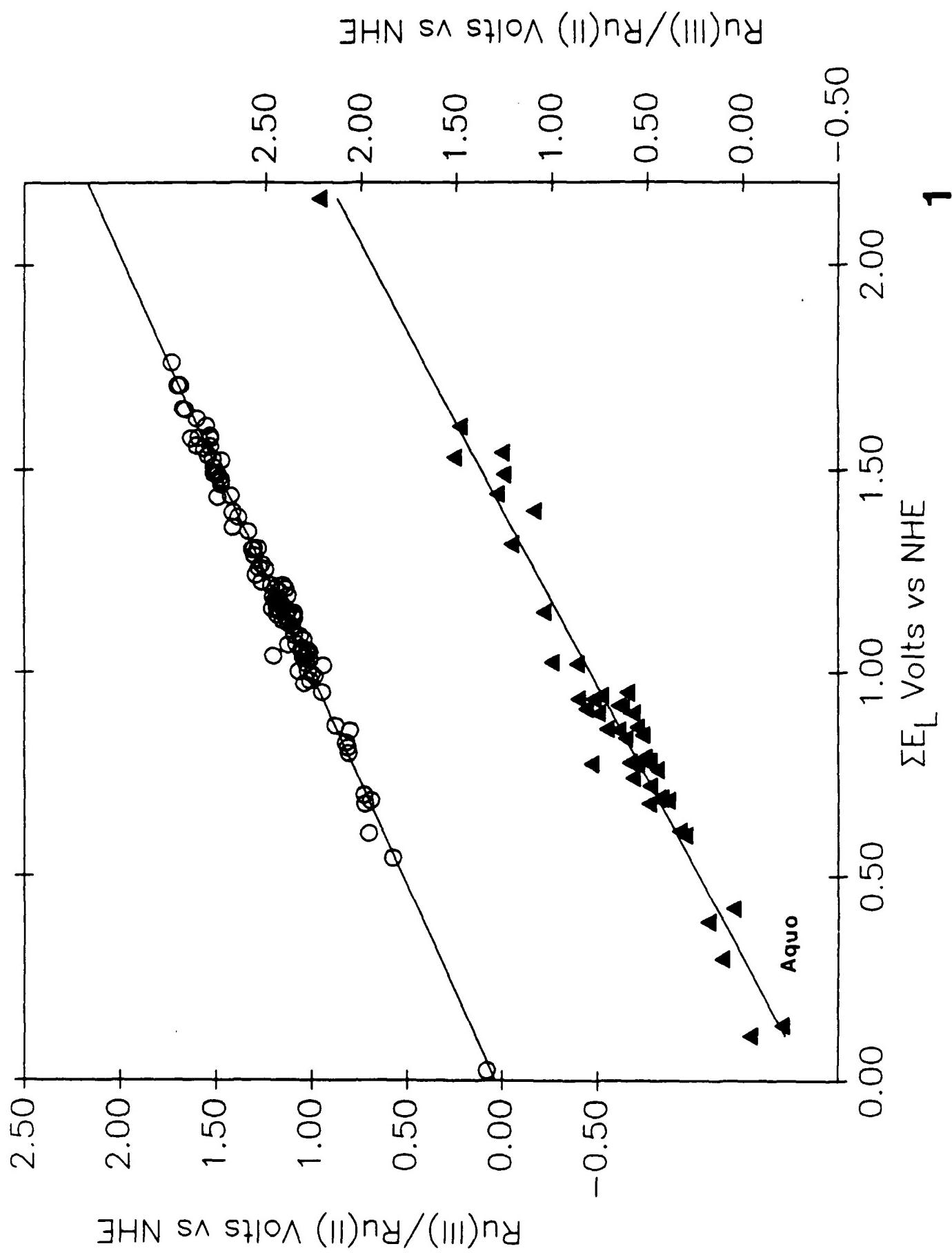
M(por)X	TPP		TPF		OEP		
	Mn(III)/Mn(II) obs.	Cal.	Fe(III)/Fe(II) obs.	Cal.	Fe(III)/Fe(II) obs.	cal.	ΣE_L
fluoride			-0.26	-0.31	-0.39	-0.43	-0.42
perchlorate	0.08	0.07	0.46	0.44	0.34	0.33	0.35
bromide	-0.02	-0.04	0.03	0.01	-0.1	-0.11	-0.22
azide	-0.10	-0.07	-0.18	-0.12	-0.28	-0.24	-0.30
chloride	-0.05	-0.04	-0.05	-0.03	-0.18	-0.15	-0.24
iodide	0.00	-0.04					-0.24
thiocyanate	-0.01	0.03	0.28	0.27			-0.06

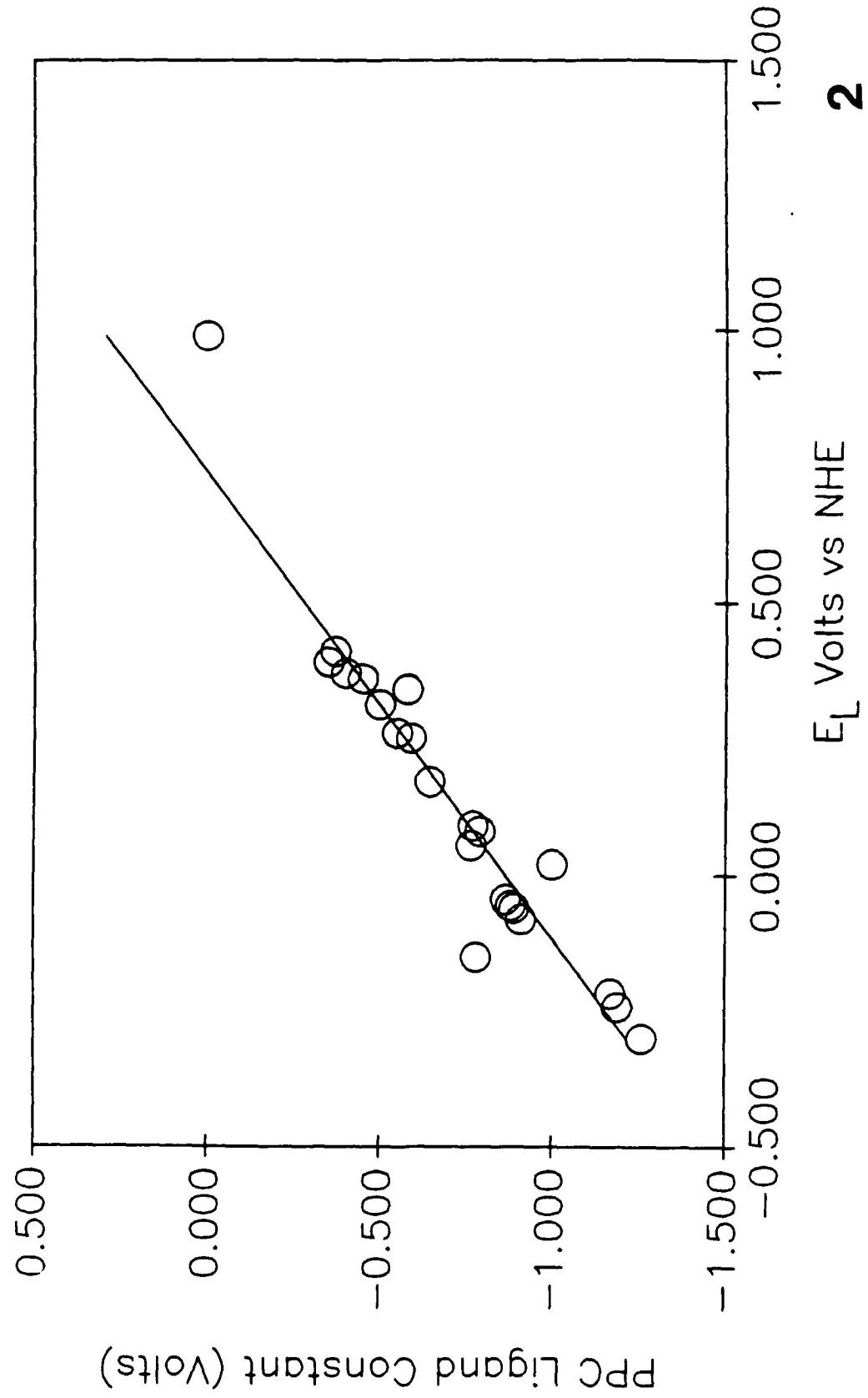
Figure Legends

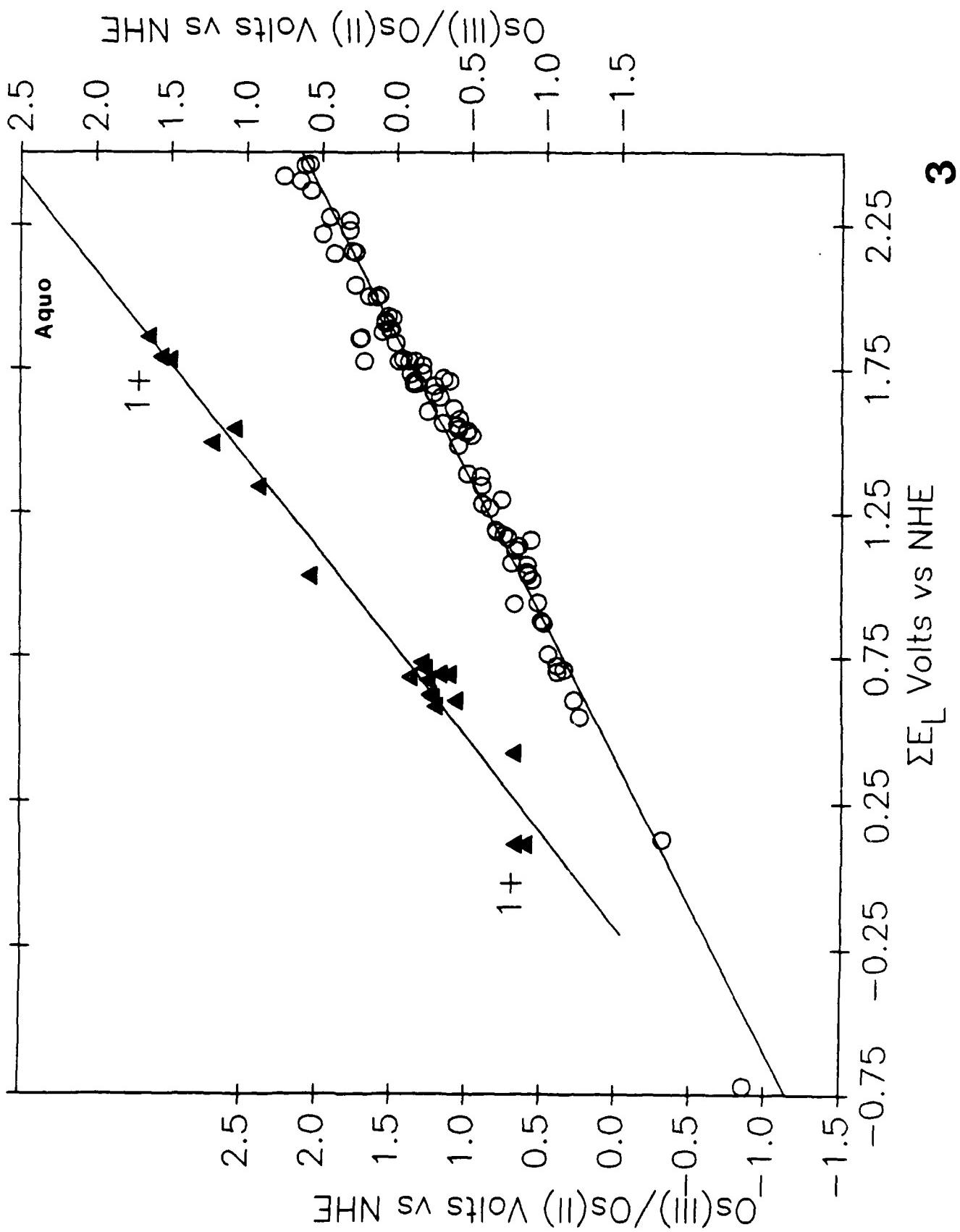
1. Plot of observed Ru(III)/Ru(II) potentials for $\text{RuX}_x\text{Y}_y\text{Z}_z$ complexes against ΣE_L . Upper (open circles): measured in organic phase solvent, are referred to left-hand Y axis. Lower (closed triangles): measured in water, and referred to right-hand Y axis. All data are vs NHE. None of the complexes here plotted were used to derive $E_L(L)$ values. For a listing of the data plotted here and in subsequent Figures, and for the relevant references, please see Appendix.
2. Plot of Picket/Fletcher ligand parameters against corresponding $E_L(L)$ values.
3. Plot of observed Os(III)/Os(II) potentials for $\text{OsX}_x\text{Y}_y\text{Z}_z$ complexes against ΣE_L . Lower (open circles): measured in organic phase solvent, are referred to left-hand Y axis. Upper (closed triangles): measured in water, and referred to right-hand Y axis.
4. Plot of observed Cr(III)/Cr(II) potentials in organic phase solvent, against ΣE_L . The open squares (upper right) represent six coordinate, low spin (LS) chromium(II) species all of which carry a net (2+) charge except for those indicated to carry (0) or (2-) charge. The closed circles (lower left) represent six coordinate high spin (HS) chromium(II) species all of which carry a (1-) charge except for those indicated with (1+) or (2+) charge. The open triangles (center left) represent six coordinate XYCr(TPP) species (TPP = tetraphenylporphyrin). In this figure and those which follow, the charge refers to the lower oxidation state complex.
5. (Upper) Plot of observed Fe(III)/Fe(II) potentials in water, for six coordinate, low spin iron(II) complexes against ΣE_L . The open triangles represent net (2+) species except for those marked with (0) or (2-) charges. The species represented by open circles all carry (3-) net charge. The closed circle is a 4- charged species. (Lower) Plot of observed Cr(III)/Cr(II) potentials in water, for six coordinate, low spin chromium(II) complexes against ΣE_L . All species carry a (2+) charge except for the (4-) species as indicated.
6. Plots of observed Fe(III)/Fe(II) potentials in organic phase solvent, against ΣE_L . Upper right: low spin (LS, both Fe(III) and Fe(II)) complexes; the filled triangles represent a range of (2+) species except where otherwise indicated. The filled circles are $\text{Fe}(\text{DMG-BF}_2)\text{XY}$ species (see text). The open circles are L_2FeTPP species (see Text). Lower left: (Open triangles), high spin (HS, both Fe(III) and Fe(II)) six coordinate complexes of (1-) charge.
7. Plot of the Mn(II)/Mn(I) potentials in organic phase solvent for a variety of organometallic, six coordinate, manganese species, versus ΣE_L . Upper data set: (Right-hand Y axis) Raw ΣE_L data uncorrected for the specific isomer involved. Lower data set: (Left hand Y axis) An isomer correction for carbon monoxide and isonitrile ligands is included. The open circles are carbonyl complexes which do not

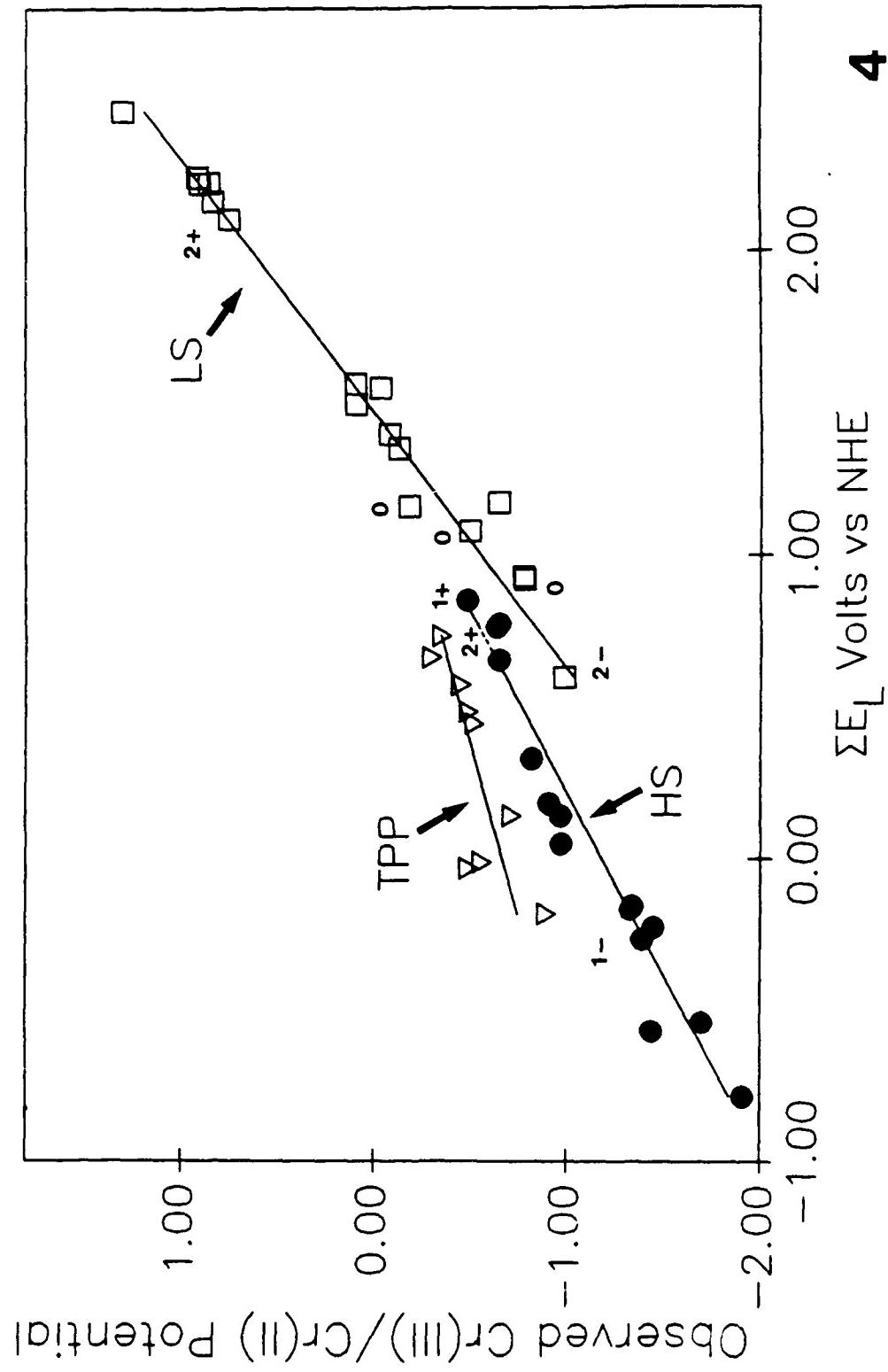
contain an isonitrile ligand. The closed circles are complexes which do contain at least one isonitrile ligand.

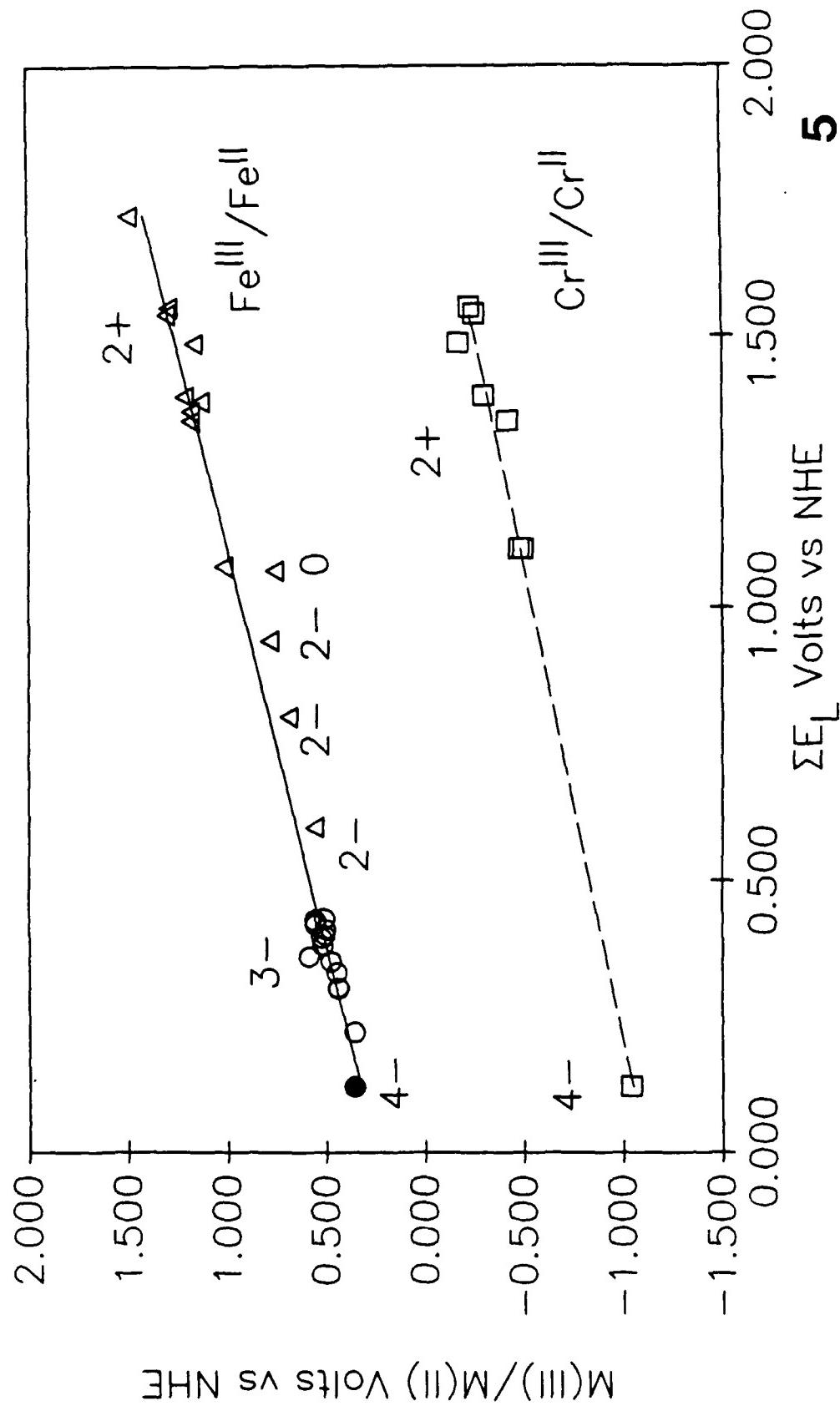
8. Lower data set: (Left hand Y axis, open circles) A plot of the Cr(I)/Cr(0) potentials in organic phase solvent for a variety of organometallic, six coordinate, chromium species, versus ΣE_L , including an isomer correction for carbon monoxide or isonitrile ligands.
Upper data set: (Right hand Y axis, closed triangles) A plot of the Mo(I)/Mo(0) potentials in organic phase solvent for a variety of organometallic, six coordinate, molybdenum species, versus ΣE_L (not isomer corrected, see text).
9. Plots of redox data for six coordinate Nb(V)/Nb(IV) (upper, open squares), Nb(IV)/Nb(III) (lower, open squares), Ta(V)/Ta(IV) (open circles), and Re(IV)/Re(III) (open triangles) versus ΣE_L , as annotated.
10. Plots of some redox data for five coordinate macrocyclic species versus ΣE_L , as annotated. XFeTPP (open triangles); XMnTPP (open circles); XFeOEP (closed triangles). (OEP = octaethylporphyrin).

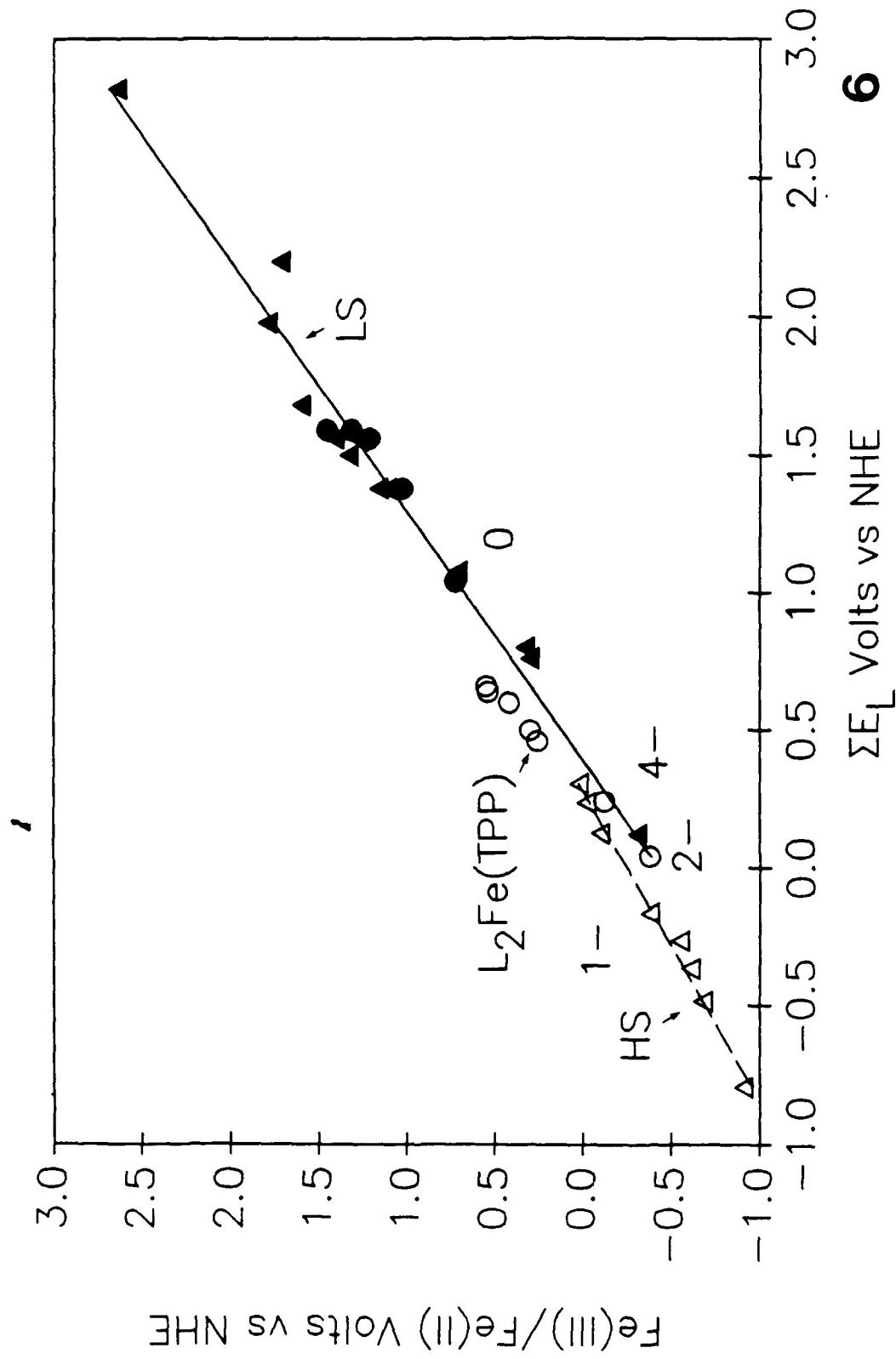


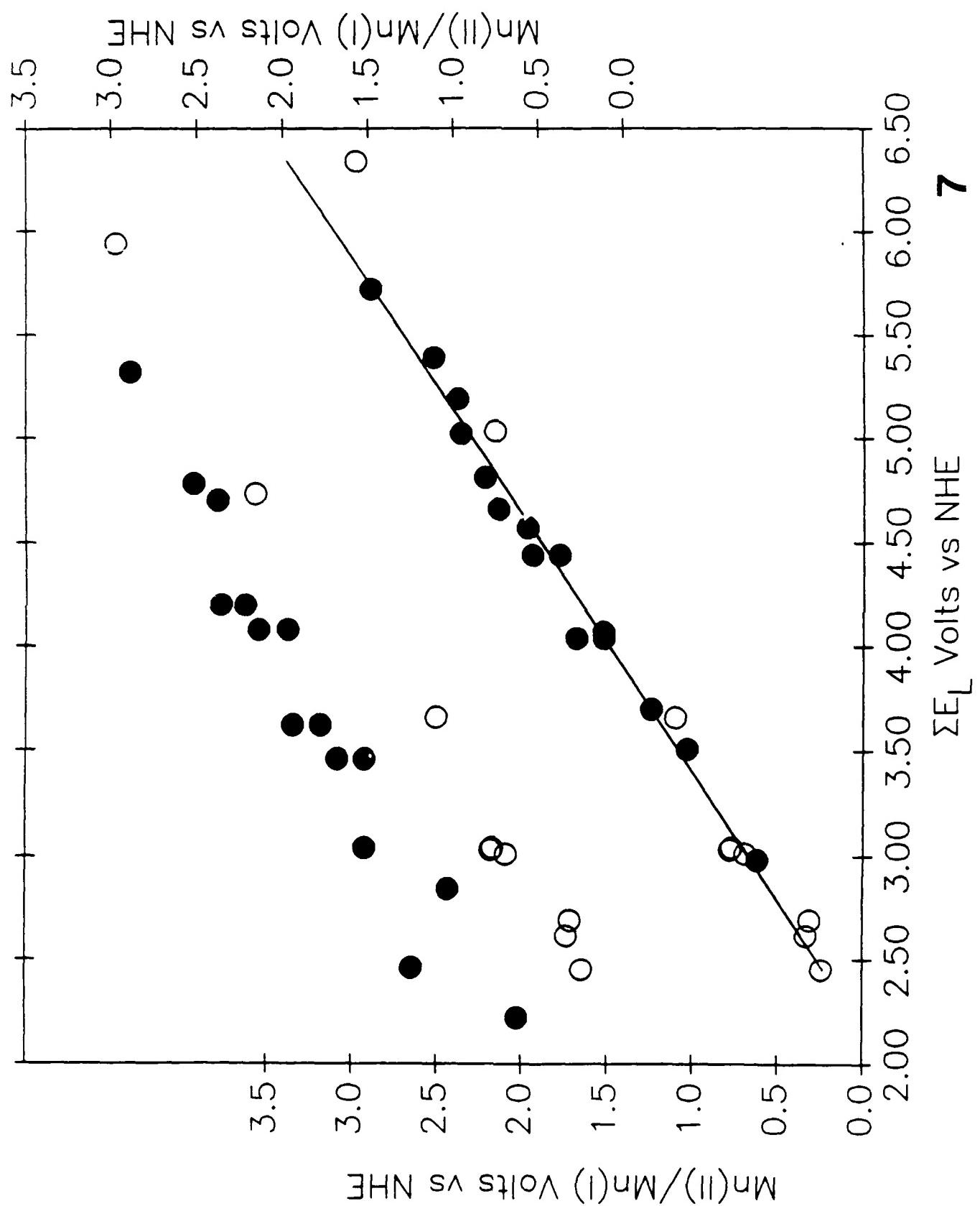


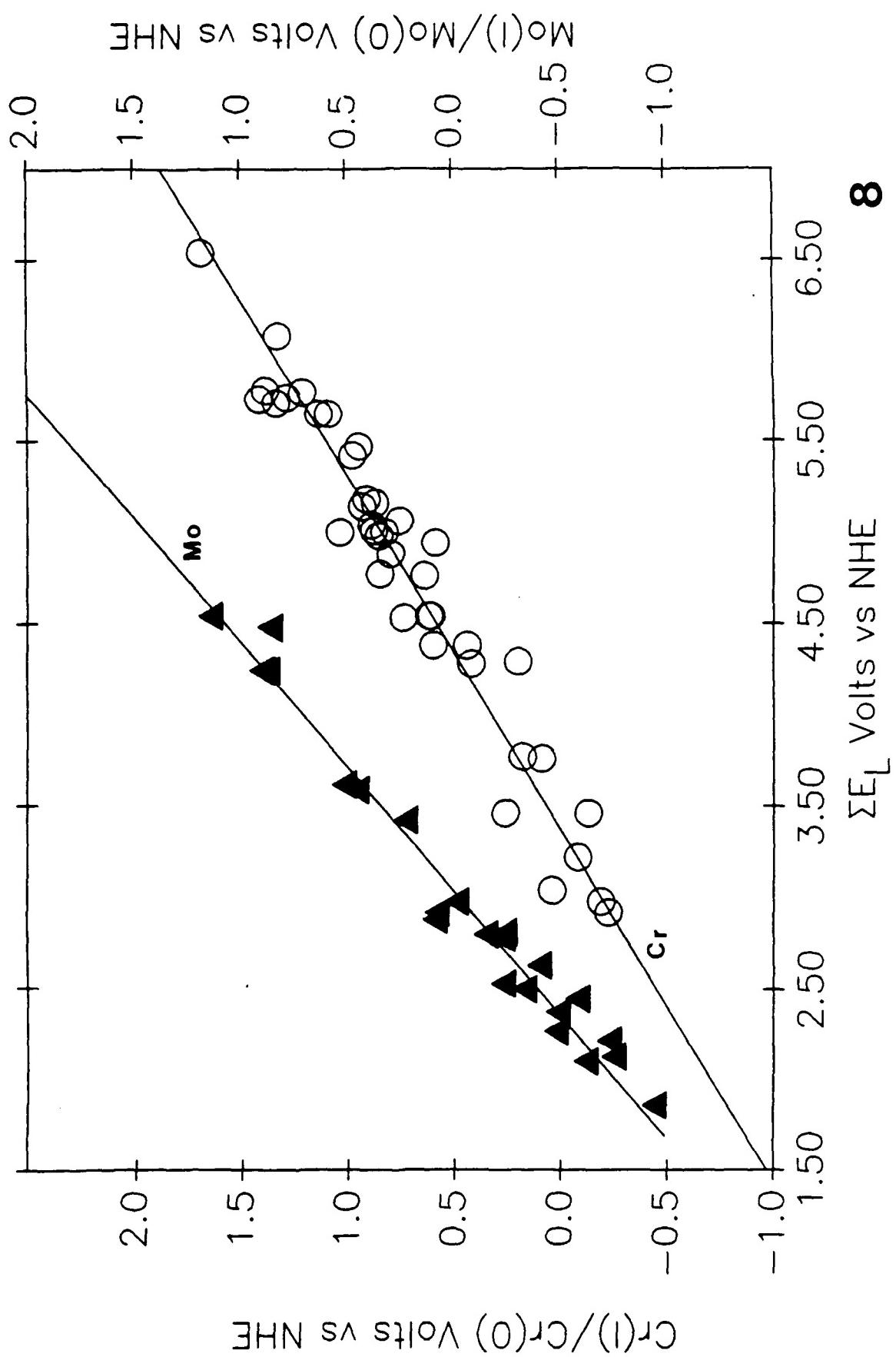


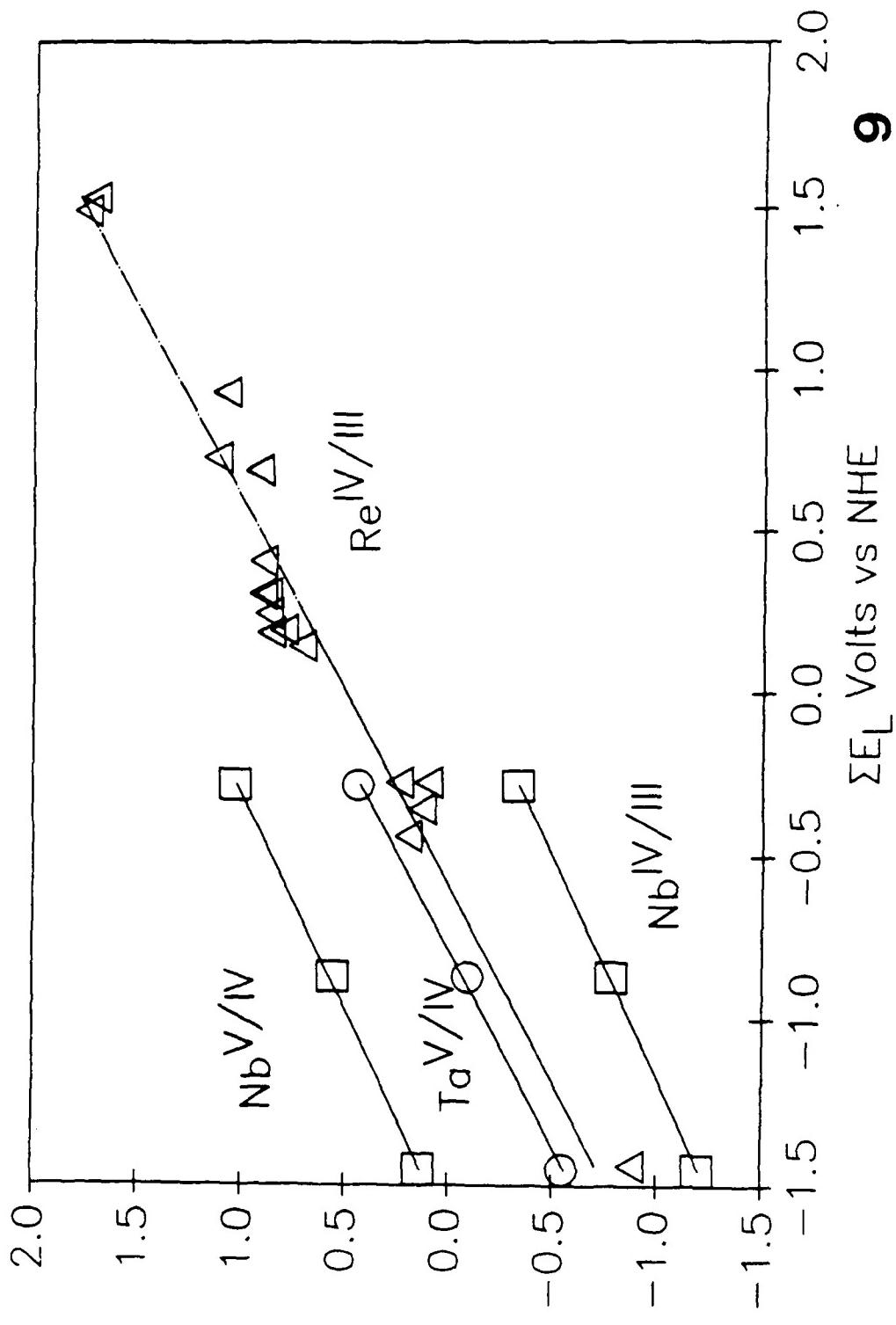












Metal Redox Potential vs NHE

9

